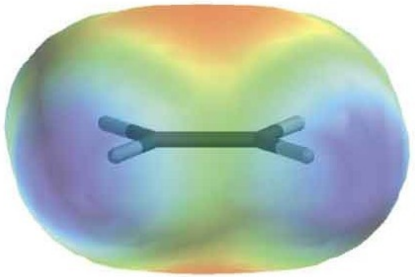
Organic Chemistry, 7th Edition

L. G. Wade, Jr.



Chapter 7

Structure and Synthesis of Alkenes

Chapter 8

Reactions of Alkenes

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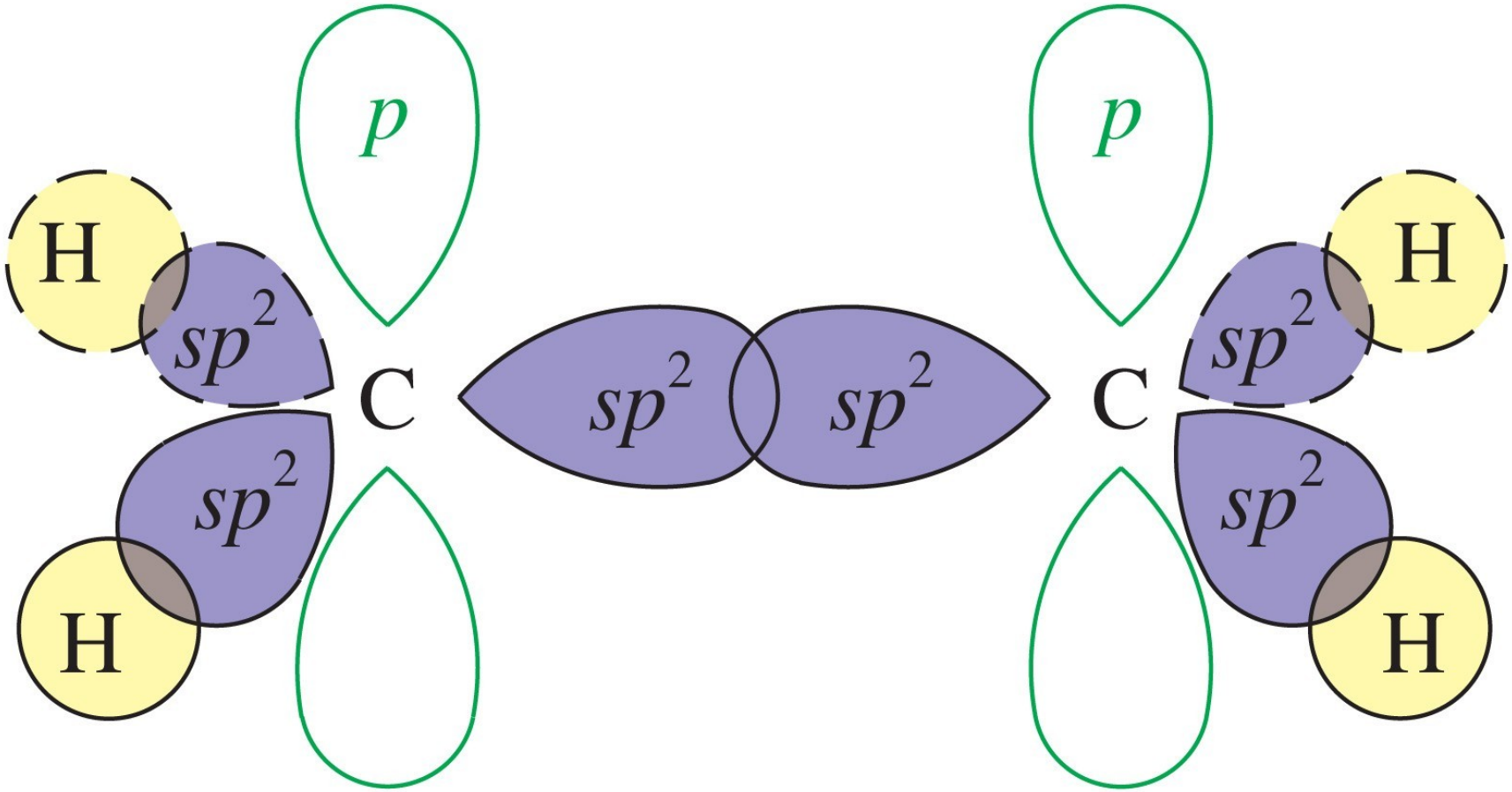
Sigma Bonds of



sigma bonding orbitals of ethylene

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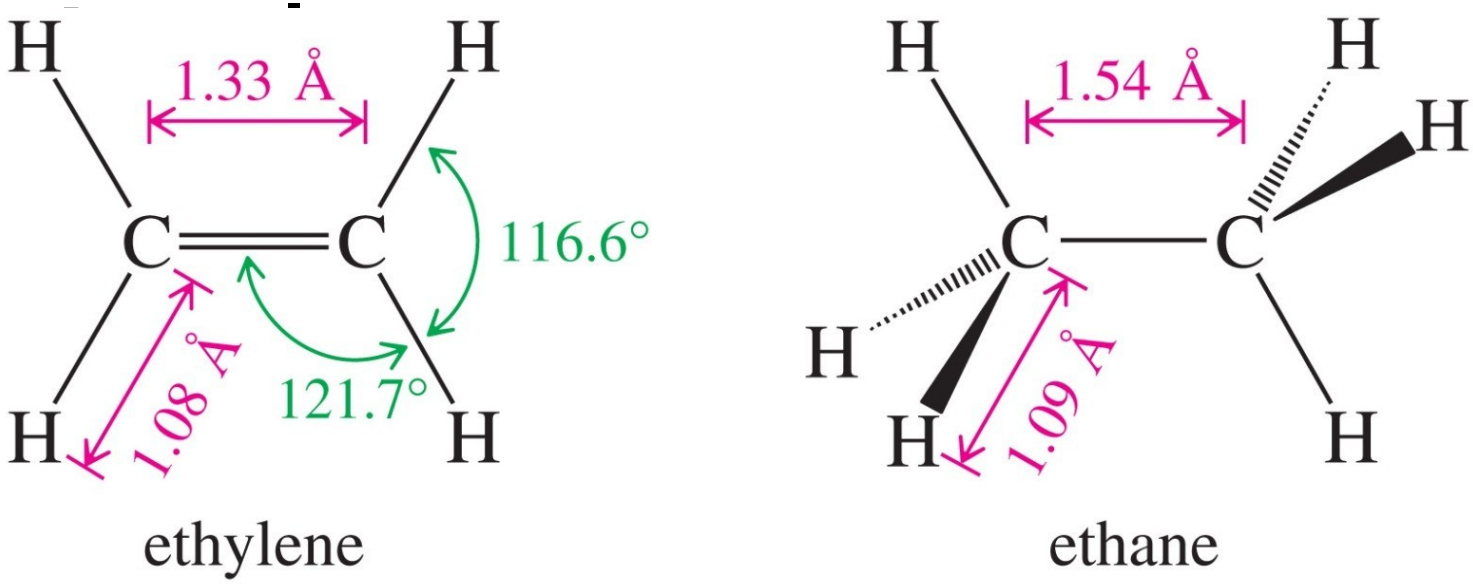
Bond Lengths and



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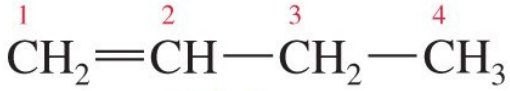
- *sp*2 hybrid orbitals have more *s* character than the *sp*3 hybrid orbitals.
- Pi overlap brings carbon atoms closer shortening the C—C bond from 1.54 Å in alkanes down to 1.33 Å in alkenes

IUPAC Nomenclature

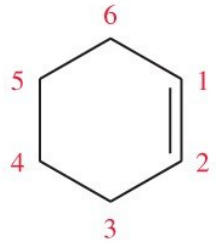
- Find the longest continuous carbon chain that includes the double-bonded carbons.
- -*ane* changes to -*ene*.
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between Carbon 1 and Carbon 2.
- Use *di*-, *tri*-, *tetra*- before the ending "*-ene*" to specify how many double bonds are present

IUPAC and New

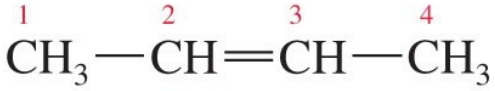


IUPAC names: 1-butene
new IUPAC names: but-1-ene

1-pentene
pent-1-ene



cyclohexene



IUPAC names: 2-butene
new IUPAC names: but-2-ene

2-pentene
pent-2-ene

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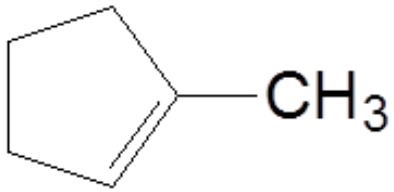
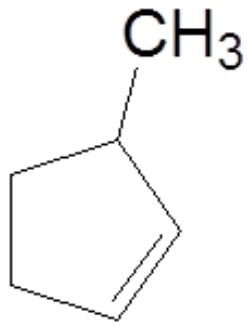
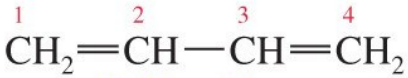


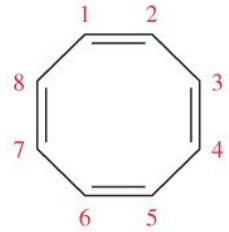
1-methylcyclopentene



3-methylcyclopentene

Multiple Double Bonds





IUPAC names: 1,3-butadiene | 1,3,5-heptatriene | 1,3,5,7-cyclooctatetraene

new IUPAC names: buta-1,3-diene | hepta-1,3,5-triene | cycloocta-1,3,5,7-tetraene

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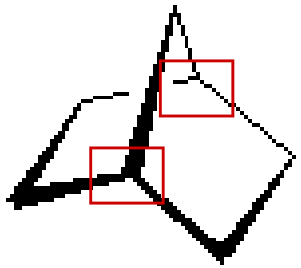
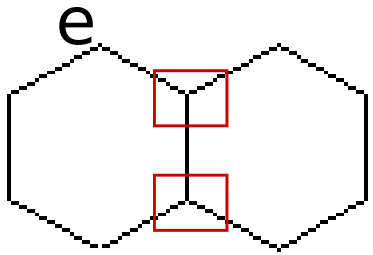
- Give the double bonds the lowest numbers possible.
- Use *di*-, *tri*-, *tetra*- before the ending "-*ene*" to specify how many double bonds are present.

Bredt's Rule

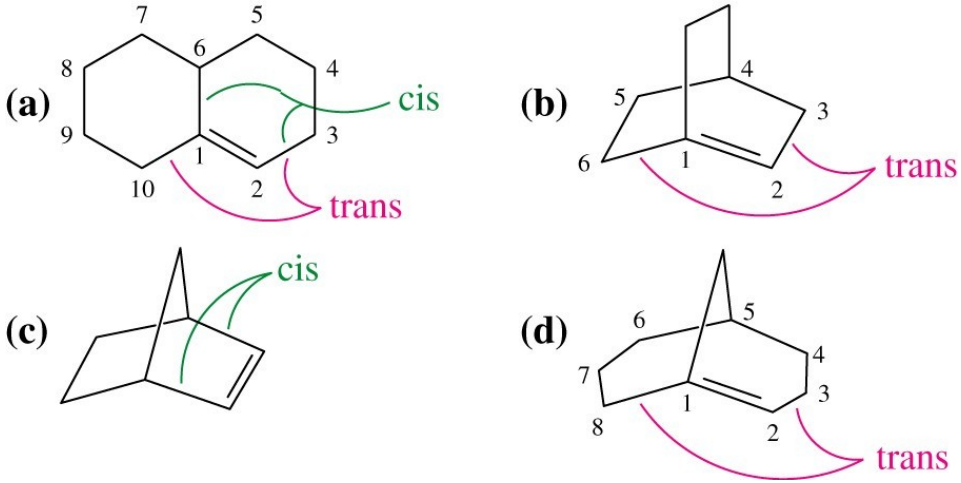
- A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbons.





Solved Problem 1

Which of the following alkenes are stable?



Soluti fina l

Compound (a) is stable. Although the double bond is at a bridgehead, it is not a bridged bicyclic system. The trans double bond is in a ten membered ring.

Compound (b) is a Bredt's rule violation and is not stable. The largest ring contains six carbon atoms, and the trans double bond cannot be stable in this bridgehead position.

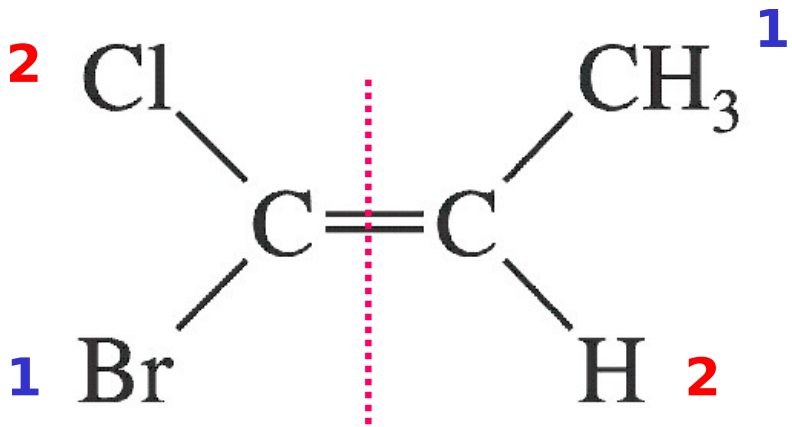
Compound (c) (norbornene) is stable. The (cis) double bond is not at a bridgehead carbon.

Compound (d) is stable. Although the double bond is at the bridgehead of a bridged bicyclic system, there is an eight-membered ring to accommodate the trans double bond.

E-*Z* Nomenclature

- Use the Cahn–Ingold–Prelog rules to assign priorities to groups attached to each carbon in the double bond.
- If high priority groups are on the same side, the name is *Z* (for *zusammen*).
- If high priority groups are on opposite sides, the name is *E* (for *entgegen*).

Exampl
e



***E*-1-bromo-1-chloropropene**

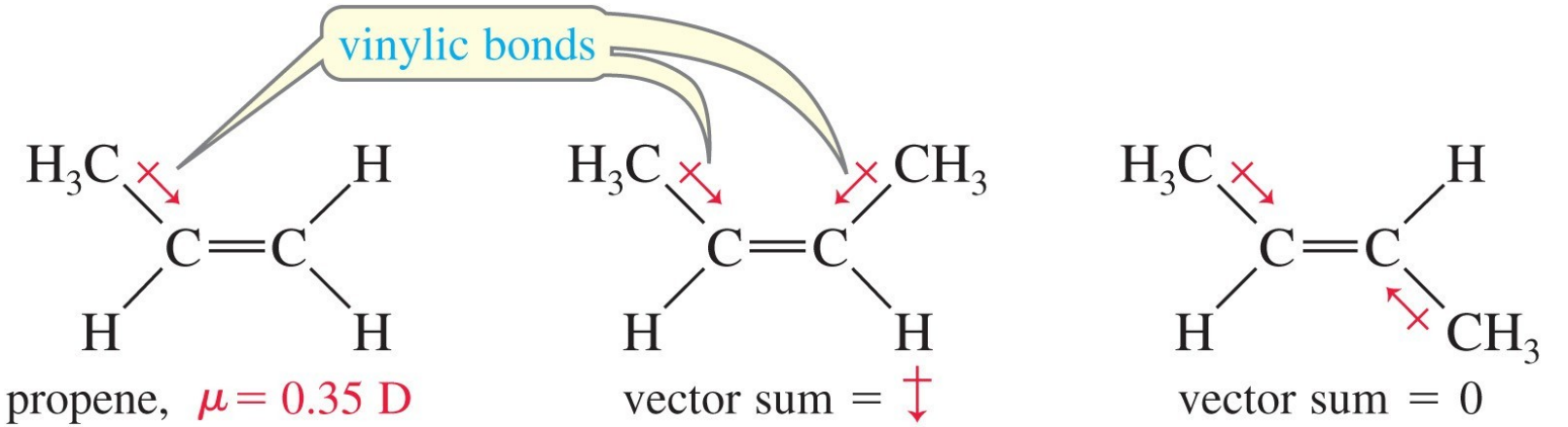
- Assign priority to the substituents according to their atomic number (1 is highest priority).
- If the highest priority groups are on opposite sides, the isomer is *E*.
- If the highest priority groups are on the same side, the isomer is *Z*.

Physical Properties of Alkenes

- Low boiling points, increasing with mass.
- Branched alkenes have lower boiling points.
- Less dense than water.
- Slightly polar:
  - Pi bond is polarizable, so instantaneous dipole– dipole interactions occur.
  - Alkyl groups are electron-donating toward the pi bond, so may have a small dipole moment.

Polarity and Dipole Moments of Alkenes

- Cis alkenes have a greater dipole moment than trans alkenes, so they will be slightly polar.
- The boiling point of cis alkenes will be higher than the trans alkenes



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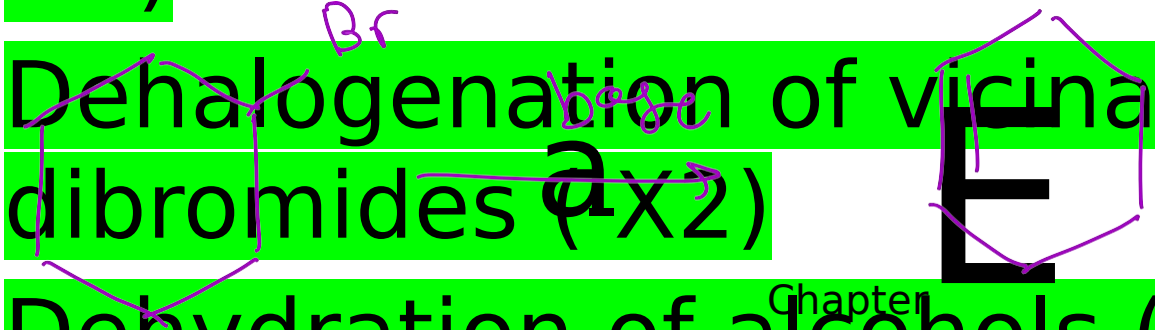
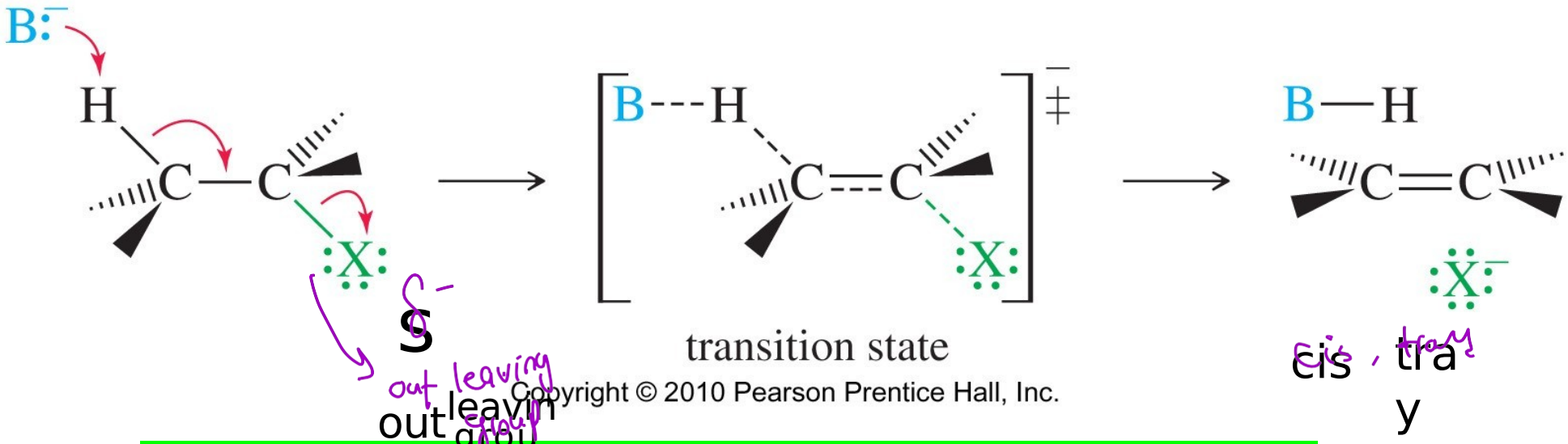
Alkene Synthesis Overview

- E2 dehydrohalogenation (-HX)
- E1 dehydrohalogenation (-HX)
- Dehalogenation of vicinal dibromides (-X2)
- Dehydration of alcohols (-H2O)



Dehydrohalogenation by the E2 Mechanism



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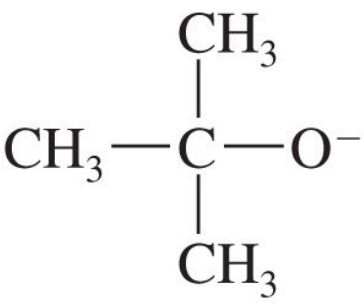
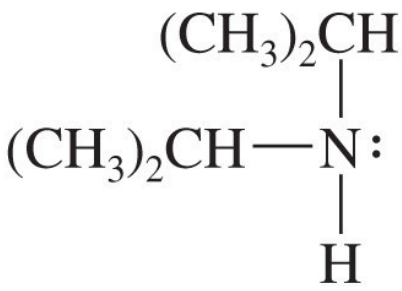
- Strong base abstracts H+ as double bond forms and X- leaves from the adjacent carbon.
- Tertiary and hindered secondary alkyl halides give good yields.

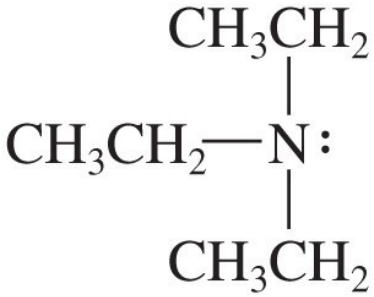
Bulky Bases for E2 Reactions



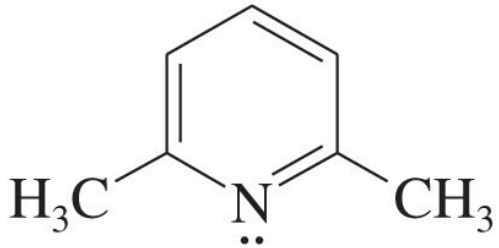
tert-butoxide



diisopropylamine



triethylamine



2,6-dimethylpyridine

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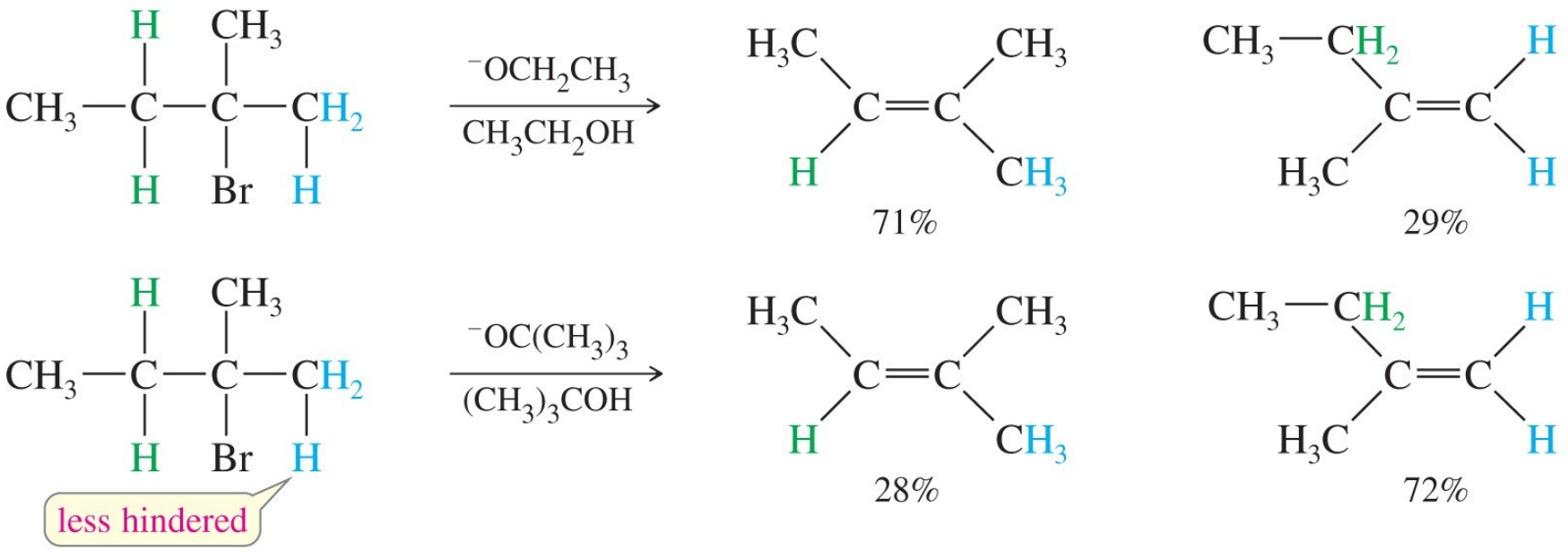
weakbabe

- If the substrate is prone to substitution, a bulky base can minimize the amount of substitution. demination
- Large alkyl groups on a bulky base hinder its approach to attack a carbon atom (substitution), yet it can easily abstract a

Hofmann Products

Bulky bases, such as potassium tert-butoxide, abstract the least hindered H+ giving the less substituted alkene as the major product (the Hofmann product).



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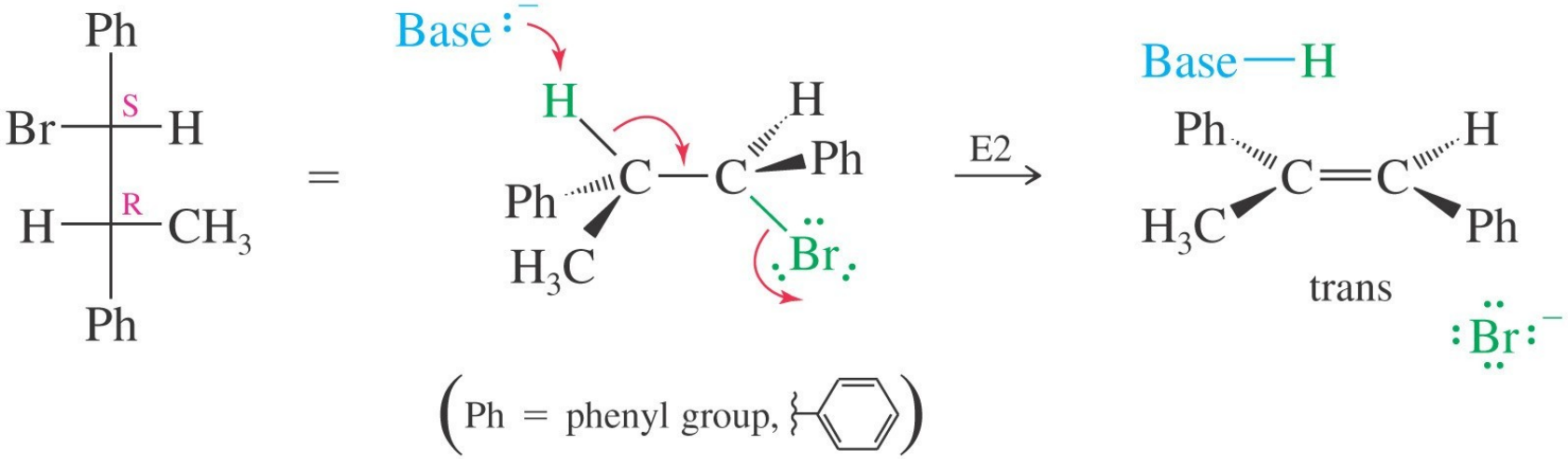
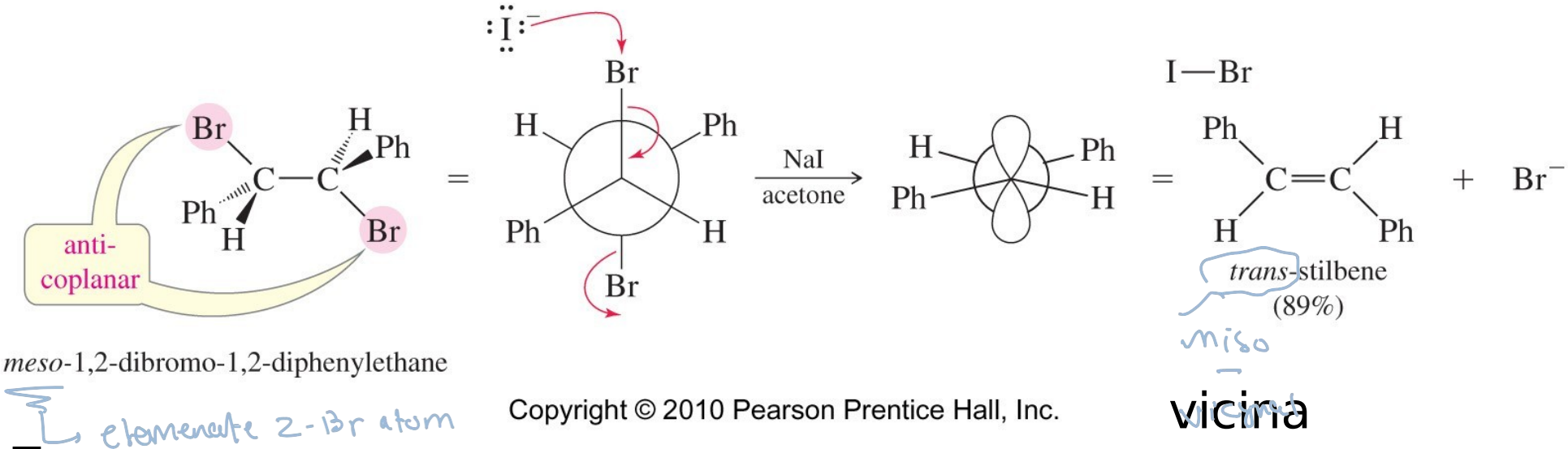
Stereochemistry of E2



- Depending on the stereochemistry of the alkyl halide, the E2 elimination may produce only the cis or only the trans isomer.
- The geometry of the product will depend on the anti- coplanar relationship between the proton and the leaving group.

Dehalogenation of Vicinal Dihalides



Es

Br atom

vicinal

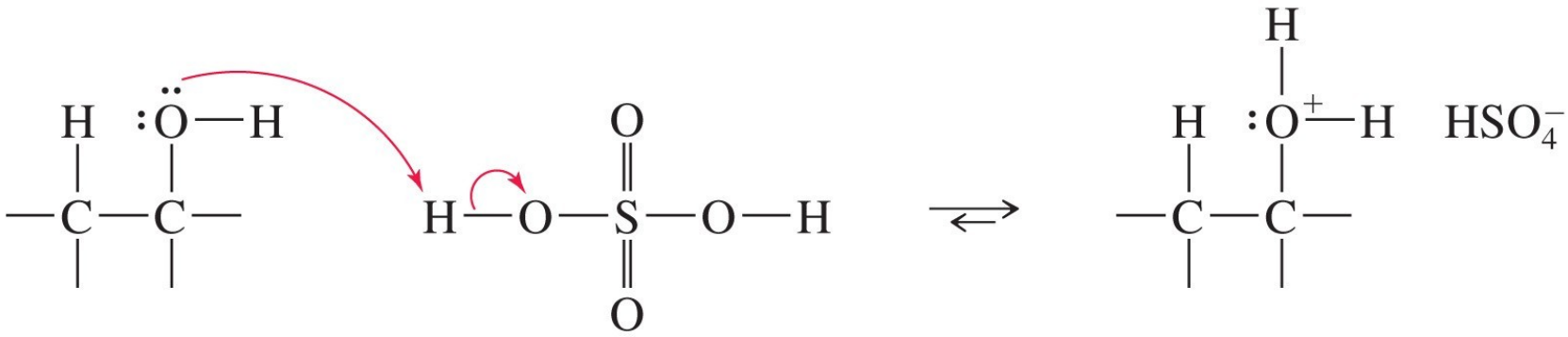
- Remove Br2 from adjacent carbons.
- Bromines must be anti-coplanar (E2).
- Use NaI in acetone or Zn in acetic acid.

Dehydration of Alcohols

- Dehydration of Alcohols:Use conc. H_2SO_4 or H_3PO_4.
- Carbocation intermediate: 3º alcohols react faster than 2º. Primary alcohols are the least reactive.
- Rearrangements are common.
- Reaction obeys Zaitsev's rule.

Dehydration Mechanism: E1

Step 1



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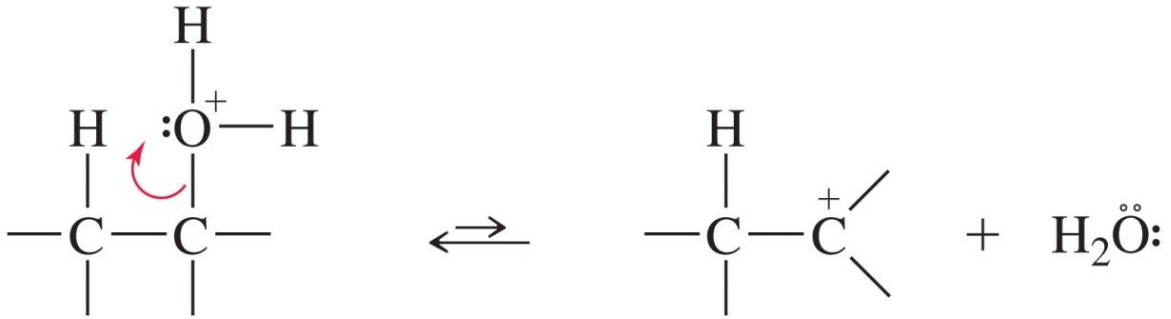
Step 2



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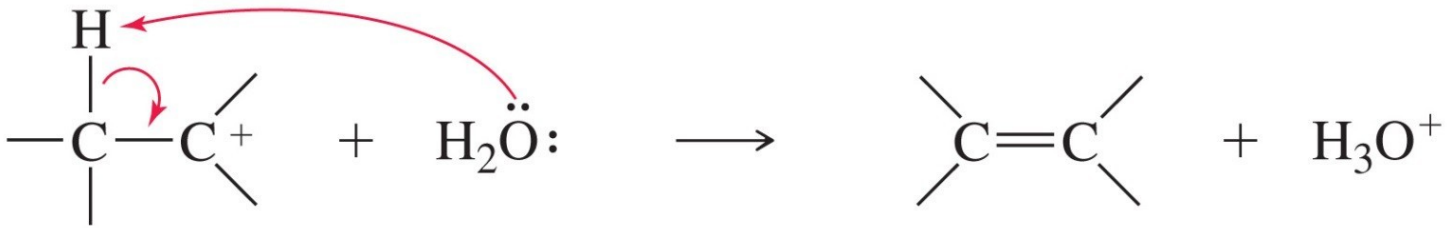
Step 3



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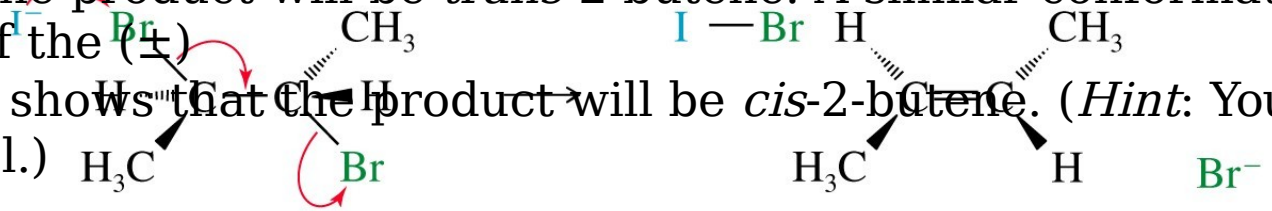
Solved Problem 2

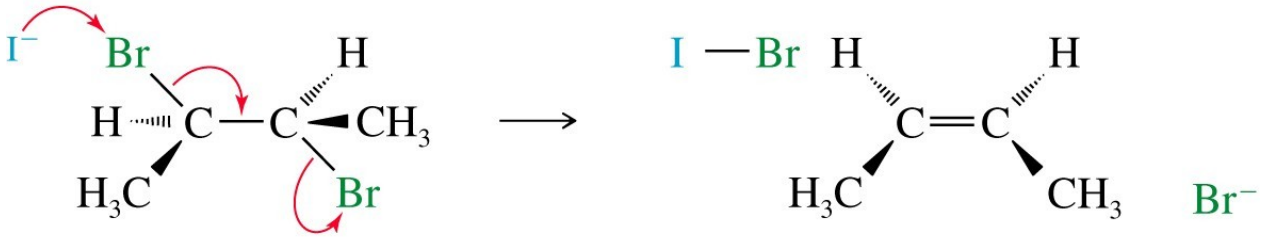
Show that the dehalogenation of 2,3-dibromobutane by iodide ion is stereospecific by showing that the two diastereomers of the starting material give different diastereomers of the product.

Solution

Rotating *meso*-2,3-dibromobutane into a conformation where the bromine atoms are anti and coplanar, we find that the product will be *trans*-2-butene. A similar conformation of either enantiomer of the (±) diastereomer shows that the product will be *cis*-2-butene. (*Hint*: Your models will be helpful.)



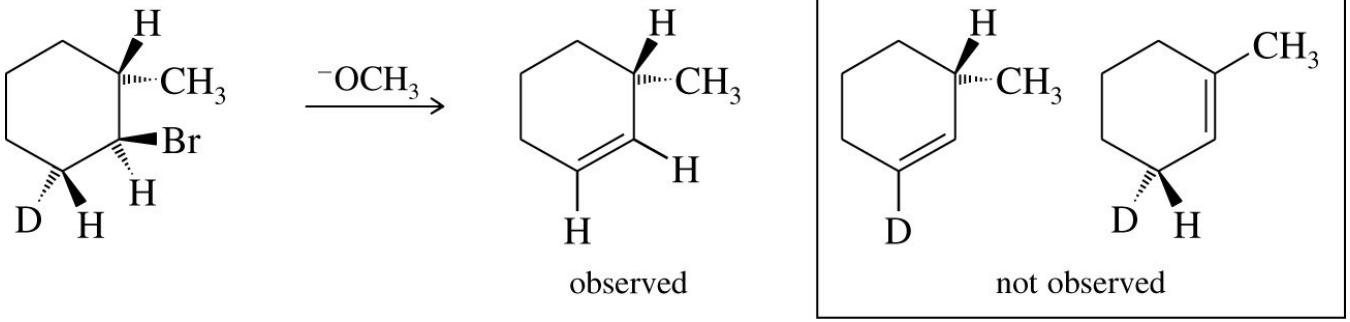
meso-2,3-dibromobutane — *trans*-2-butene



(R,R)-2,3-dibromobutane — *cis*-2-butene

Solved Problem 3

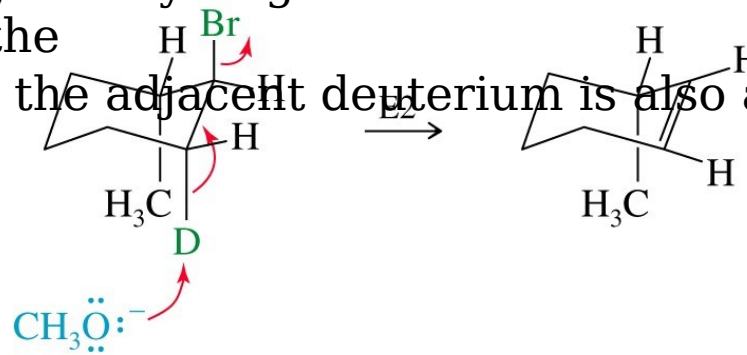
Explain why the following deuterated 1-bromo-2-methylcyclohexane undergoes dehydrohalogenation by the E2 mechanism, to give only the indicated product. Two other alkenes are not observed.



Solution

In an E2 elimination, the hydrogen atom and the leaving group must have a trans-diaxial relationship.

In this compound, only one hydrogen atom—the deuterium—is trans to the bromine atom. When the bromine atom is axial, the adjacent deuterium is also axial, providing a trans-diaxial arrangement.

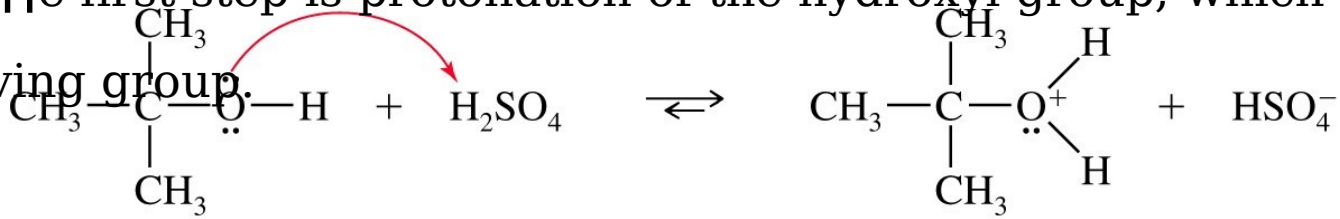


Solved Problem 4

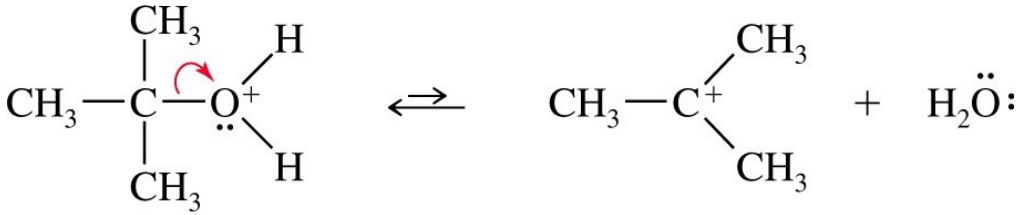
Propose a mechanism for the sulfuric acid–catalyzed dehydration of *t*-butyl alcohol.

Solution

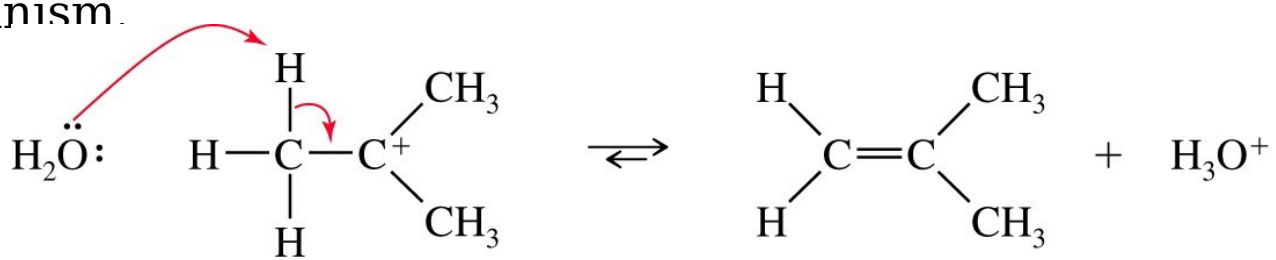
The first step is protonation of the hydroxyl group, which converts it to a good leaving group.



The second step is ionization of the protonated alcohol to give a carbocation.

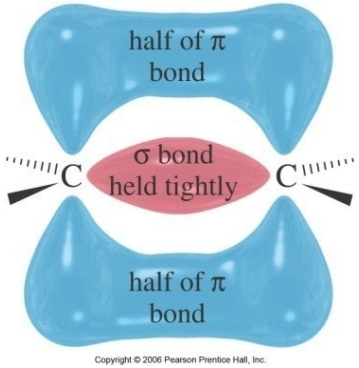


Abstraction of a proton completes the mechanism.



Bonding in Alkenes

- Electrons in pi bond are loosely held.
- The double bond acts as a nucleophile attacking electrophilic species.
- Carbocations are intermediates in the reactions.
- These reactions are called ***electrophilic additions***.



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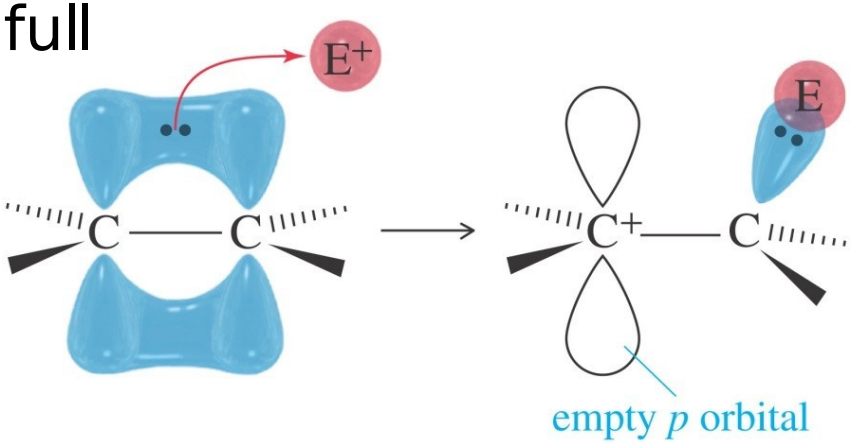
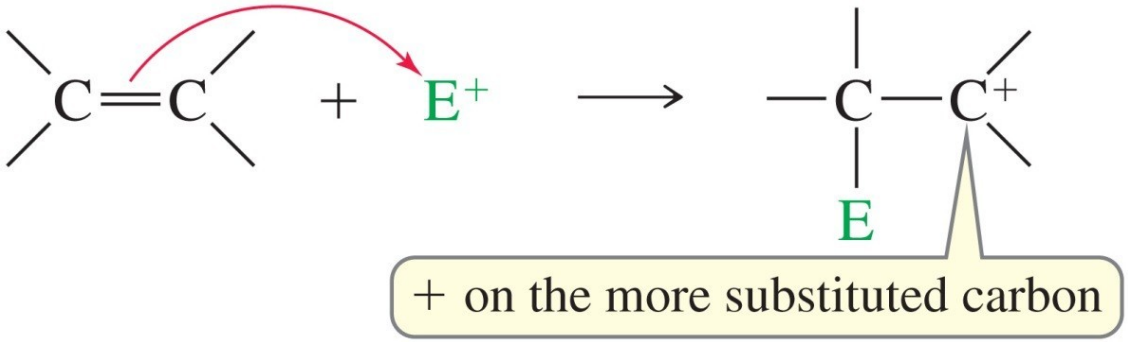


Electrophilic Addition

- Step 1: Pi electrons attack the elec



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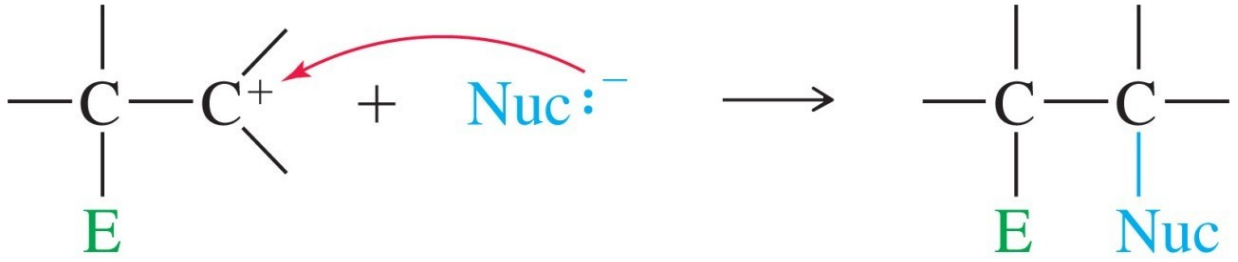
- Step 2: Nucleophile attacks the carbocation



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Types of

addition of

Result Alcohol

removal

oxidation of H

hydrogen Peroxide

Q

X

TABLE 8-1

Types of Additions to Alkenes

C=C	Type of Addition [Elements Added][a]	Product
	hydration [H_2O]	H OH
	hydrogenation [H_2], a reduction	H H
	hydroxylation [HOOH], an oxidation	OH OH
	oxidative cleavage [O_2], an oxidation	C=O O=C
	epoxidation [O], an oxidation	O
	halogenation [X_2], an oxidation	X X
	halohydrin formation [HOX], an oxidation	X OH
	HX addition [HX] (hydrohalogenation)	H X
	cyclopropanation [CH_2]	H H C

[a]These are not the reagents used but simply the groups that appear in the product.

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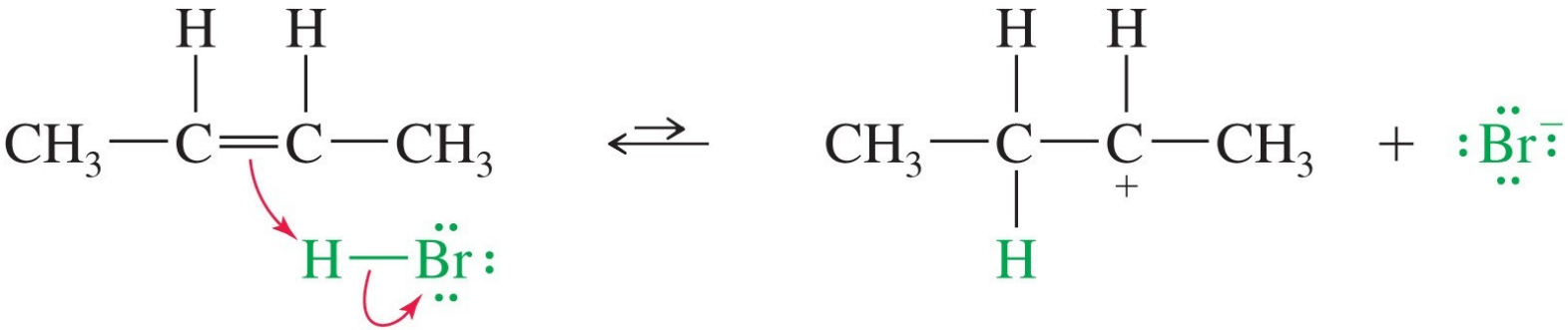
Addition of HX to Alkenes

- Step 1 is the protonation of the double bond.
- The protonation step forms the most stable carbocation possible.
- In step 2, the nucleophile attacks the carbocation, forming an alkyl halide.
- HBr, HCl, and HI can be added through this reaction.

Mechanism of Addition of HX

Step 1: Protonation of the double bond



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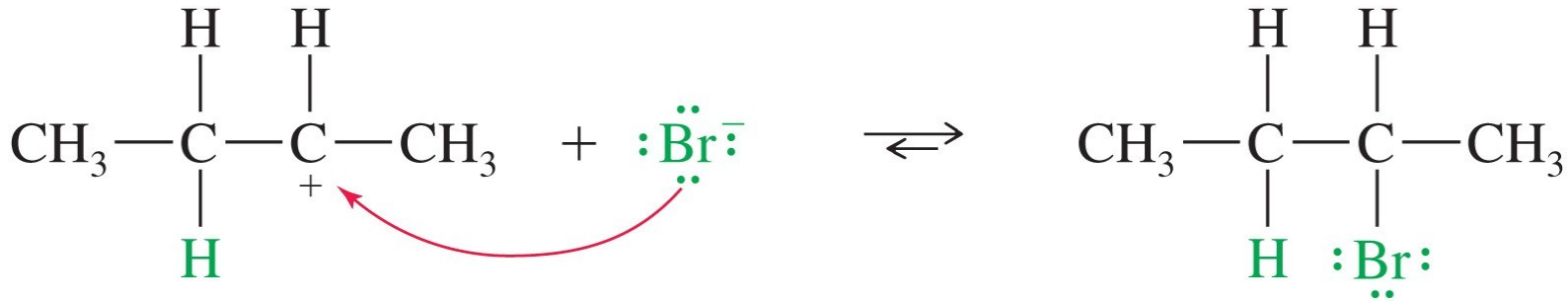
Step 2: Nucleophilic attack of the halide on the carbocation



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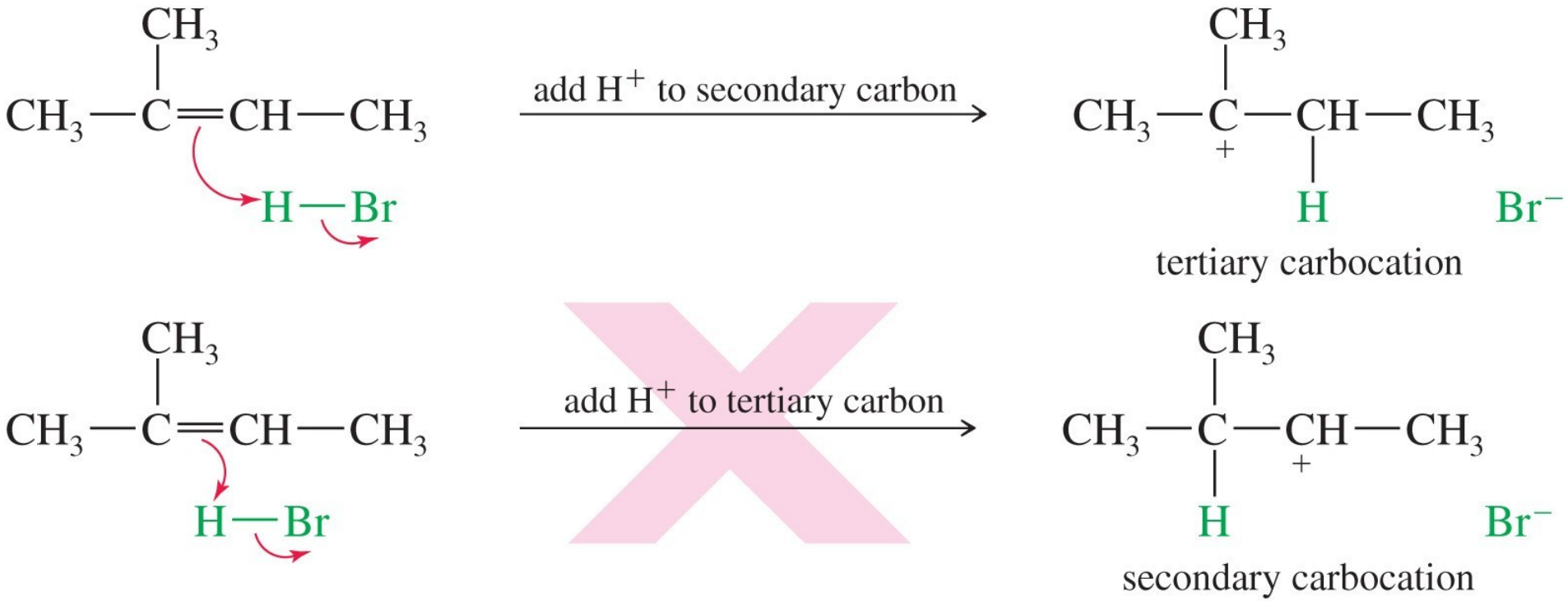
Regioselectivity

- Markovnikov's Rule: The addition of a proton to the double bond of an alkene results in a product with the acidic proton bonded to the carbon atom that already holds the greater number of hydrogens.
- Markovnikov's Rule (extended): the electrophile adds in such a way that it generates the most stable intermediate.

Markovnikov's Rule



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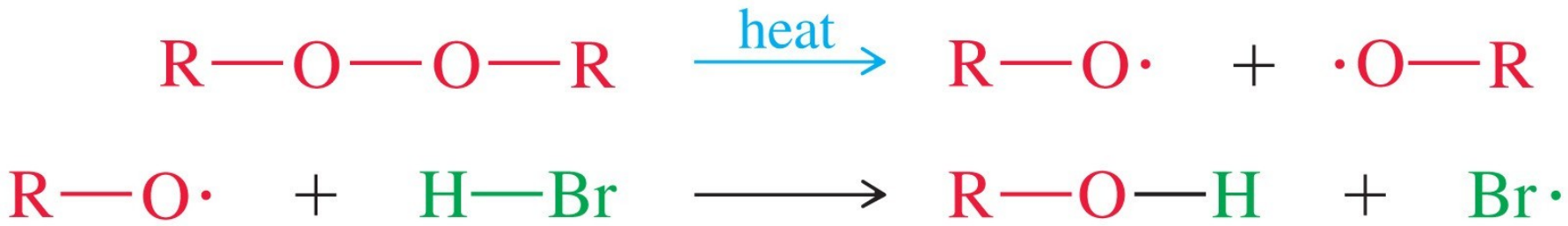
The acid proton will bond to carbon 3 in order to produce the most stable carbocation possible.

Free-Radical Addition of HBr

- In the presence of peroxides, HBr adds to an alkene to form the “anti-Markovnikov” product.
- Peroxides produce free radicals.
- Only HBr has the right bond energy.
- The HCl bond is too strong, so it will add according to Markovnikov’s rule, even in the presence of peroxide.
- The HI bond tends to break heterolytically to form ions, it too will add according to Markovnikov’s rule.

Free-Radical Initiation

- The peroxide bond breaks homolytically to form the first radical:



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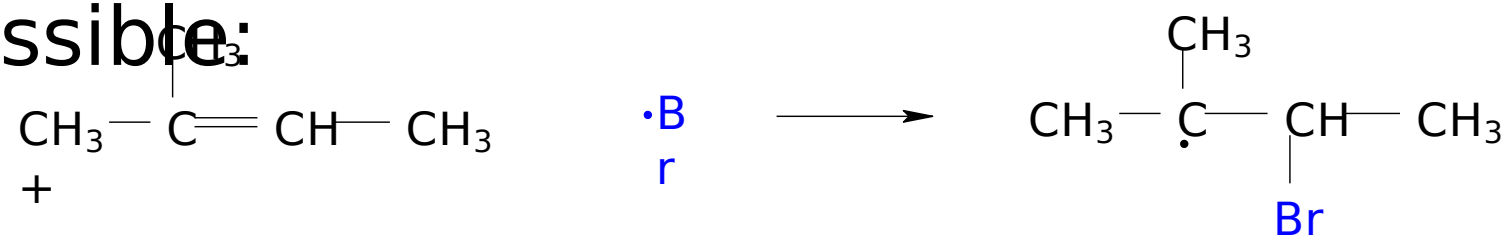
- Hydrogen is abstracted from HBr.

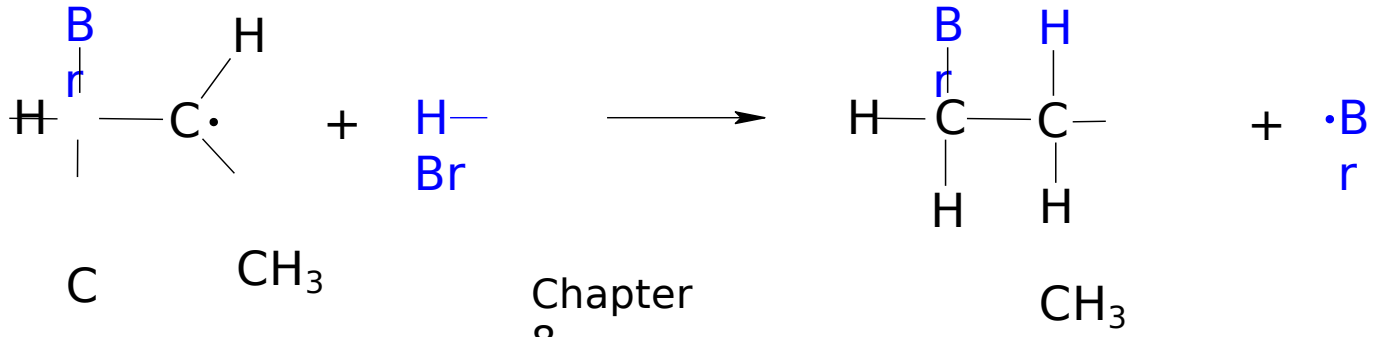
Propagation Steps

- Bromine adds to the double bond forming the most stable radical possible:

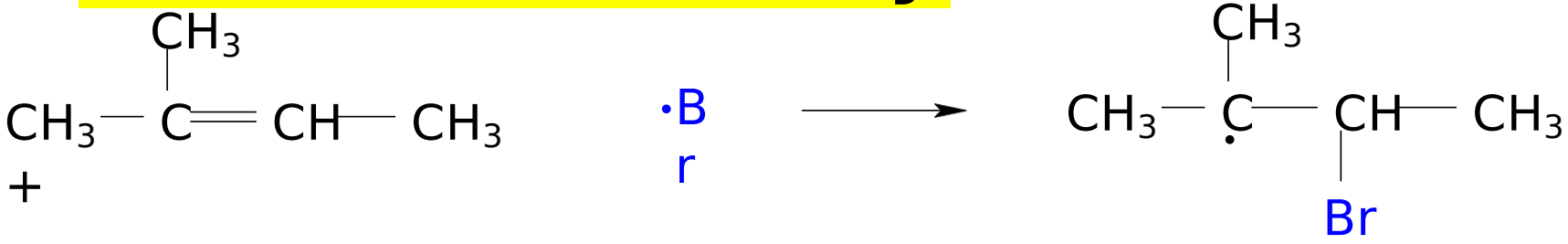


- Hydrogen is abstracted from HBr:

(more stable)

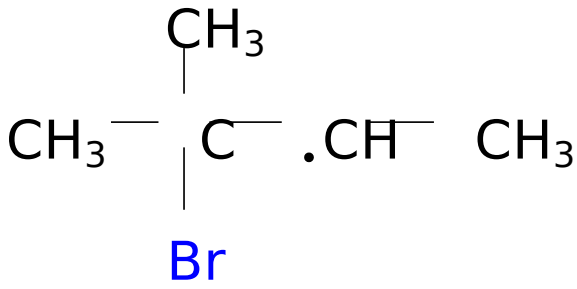


Anti-Markovnikov Stereochemistry



tertiary radical (more stable)

- The intermediate tertiary radical forms faster because it is more stable.

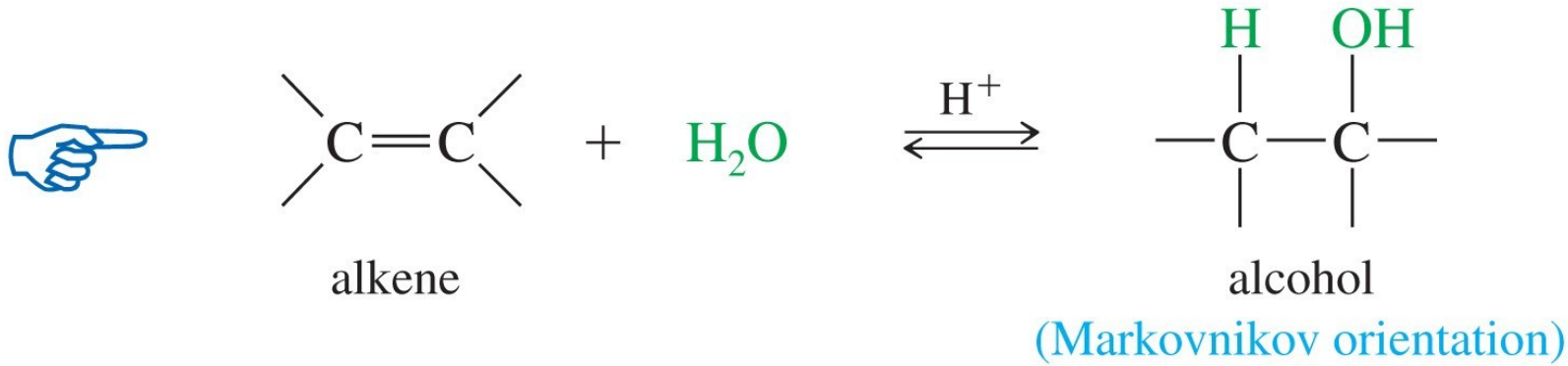


secondary radical (less stable)

not formed

Hydration of Alkenes

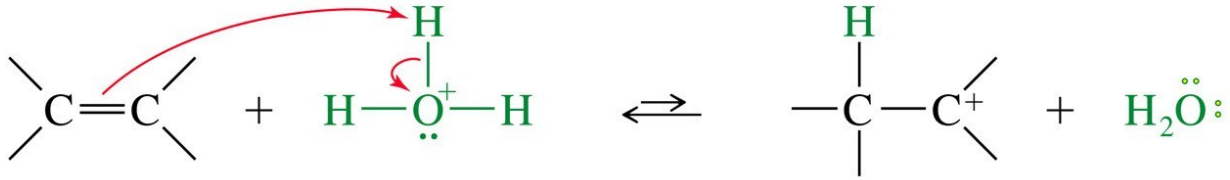
Hydration of an alkene



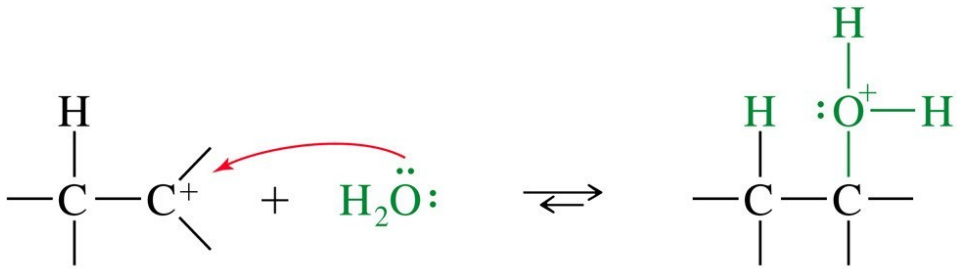
- The Markovnikov addition of water to the double bond forms an alcohol.
- This is the reverse of the dehydration of alcohol.
- Uses dilute solutions of H2SO4 or H3PO4 to drive equilibrium toward hydration.

Mechanism for

Step 1: Protonation of the double bond forms a carbocation.

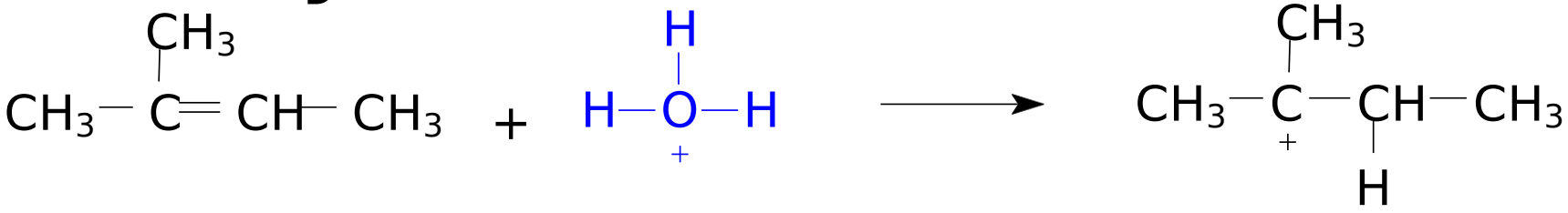


Step 2: Nucleophilic attack by water.



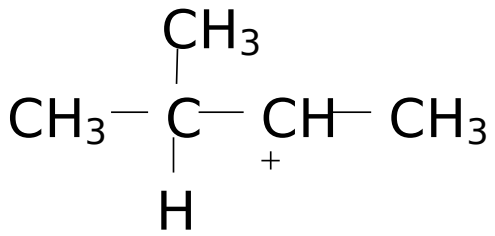
Step 3: Deprotonation to the alcohol.

Orientation of Hydration



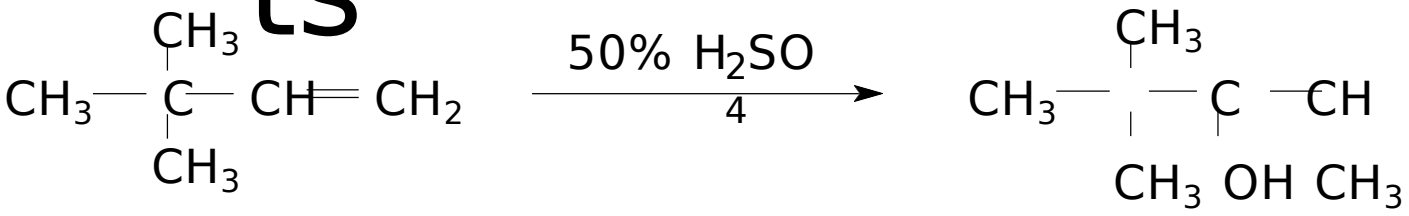
3º, more stable

The protonation follows Markovnikov's rule: The hydrogen is added to the less substituted carbon in order to form the most stable carbocation.

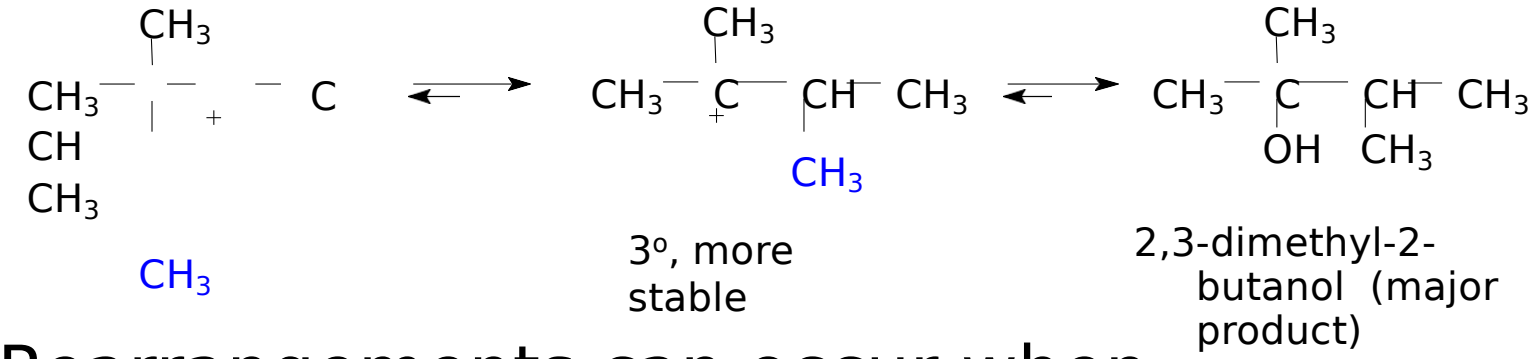


2º less stable, not formed

Rearrangements



Rearrangement:



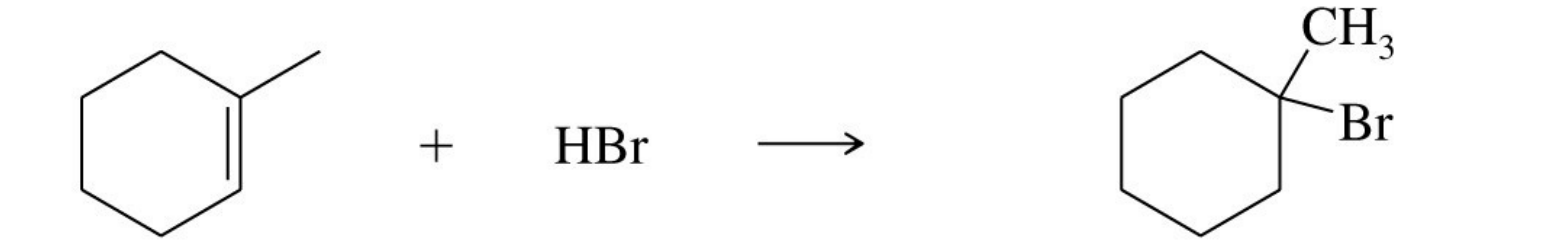
- Rearrangements can occur when there are carbocation intermediates.
- A methyl shift after protonation will produce the more stable tertiary carbocation.

Solved Problem 1

Show how you would accomplish the following synthetic conversions.
(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

Solution

This synthesis requires the addition of HBr to an alkene with Markovnikov orientation. Ionic addition of HBr gives the correct product.



1-methylcyclohexene

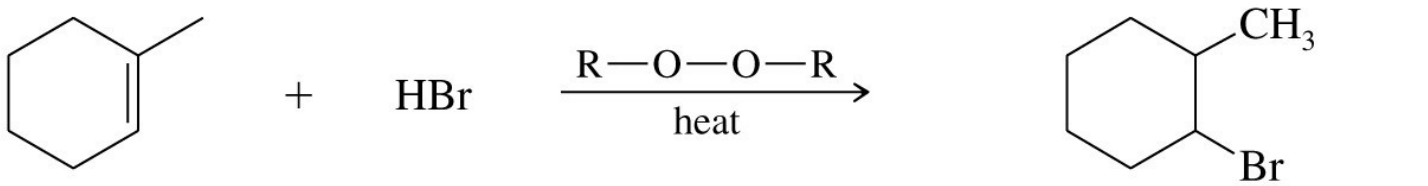
1-bromo-1-methylcyclohexane

Solved Problem 2

Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

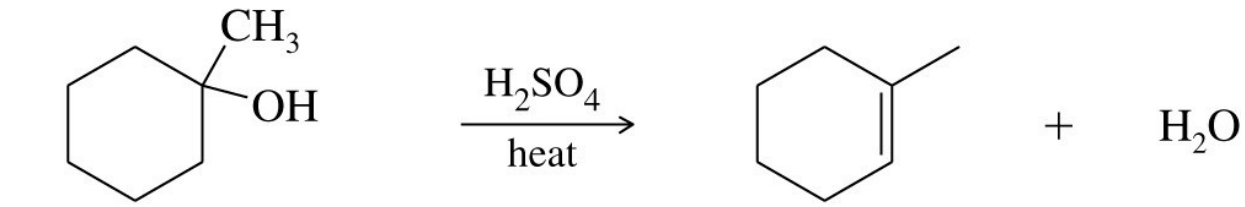
Solution

This synthesis requires the conversion of an alcohol to an alkyl bromide with the bromine atom at the neighboring carbon atom. This is the anti-Markovnikov product, which could be formed by the radical-catalyzed addition of HBr to 1-methylcyclohexene.



1-methylcyclohexene 1-bromo-2-methylcyclohexane

1-Methylcyclohexene is easily synthesized by the dehydration of 1-methylcyclohexanol. The most substituted alkene is the desired product.

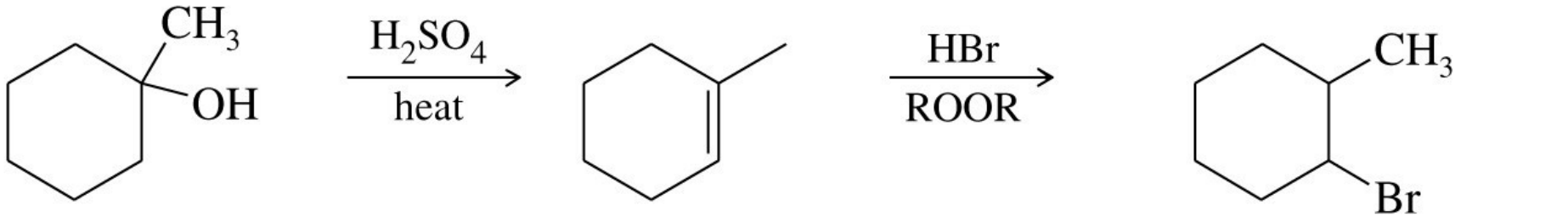


1-methylcyclohexanol 1-methylcyclohexene

Solved Problem 2 (Continued)

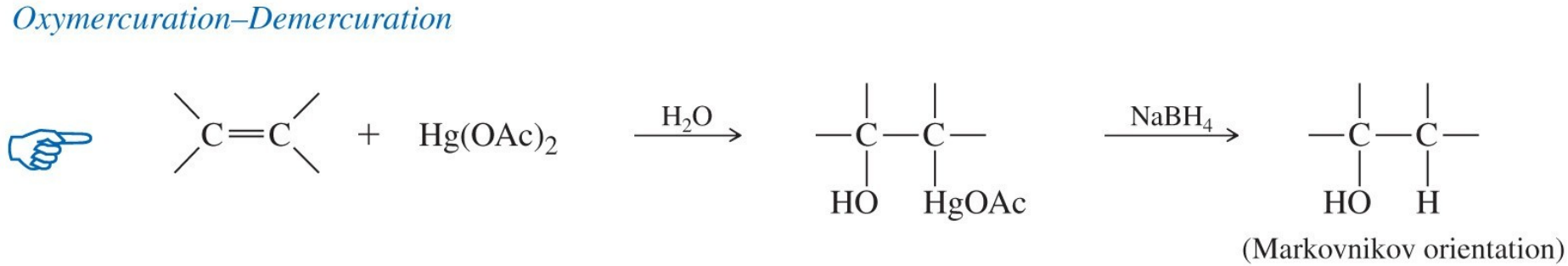
Solution (Continued)

The two-step synthesis is summarized as follows:



1-methylcyclohexanol 1-methylcyclohexene 1-bromo-2-methylcyclohexane

Oxymercuration–Demercuration Reaction



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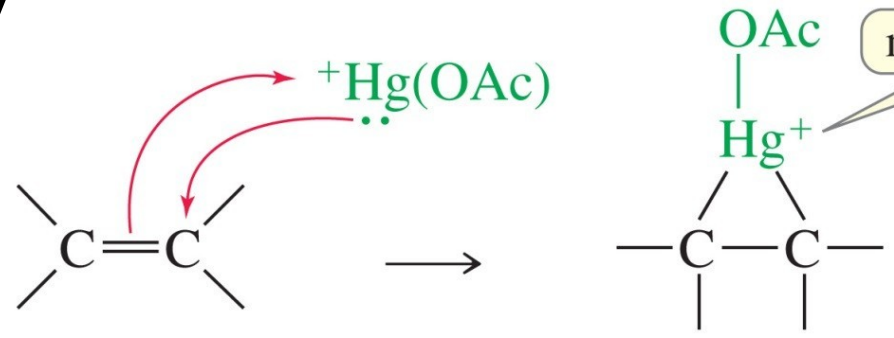
- Markovnikov addition of water to the double bond.
- No rearrangements.
- This is a two-step process.

Oxymercuration Reaction

- Reagent is mercury(II) acetate, which dissociates slightly to form +Hg(OAc).
- +Hg(OAc) is the electrophile that adds to the pi bond.
- The intermediate is a three-membered ring called the mercurinium ion.
- Overall the addition of water follows Markovnikov's rule.

Mechanism of Oxymercuration



Intermediate

no carbocation

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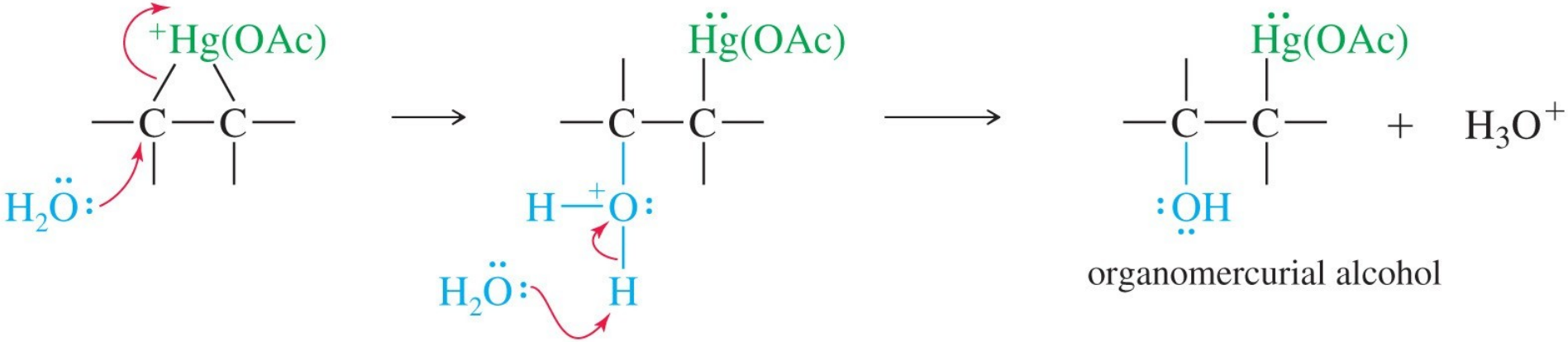

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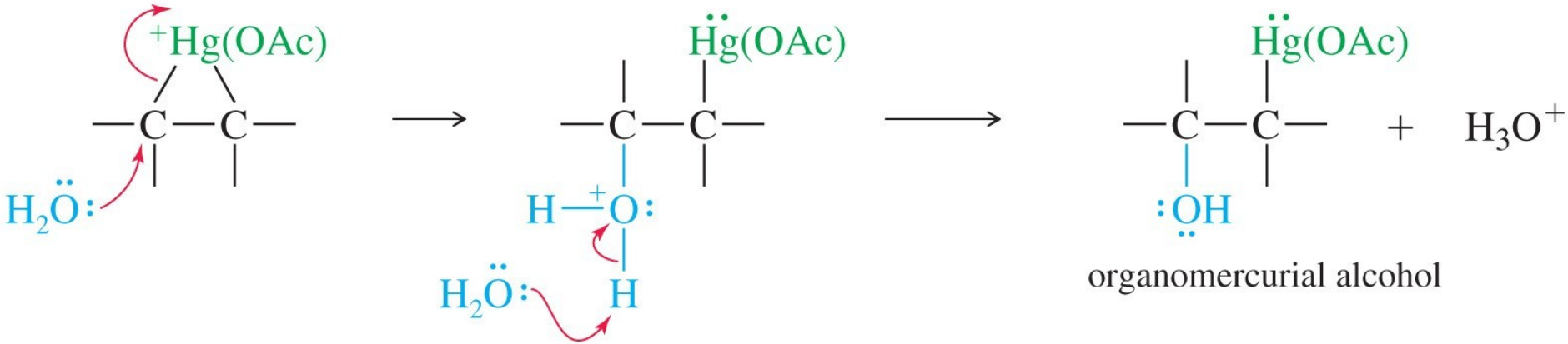
Mercurinium Ion Opening

- Water adds to the more substituted carbon to form the Markovnikov product.
- Water approaches the mercurinium ion from the side opposite the ring



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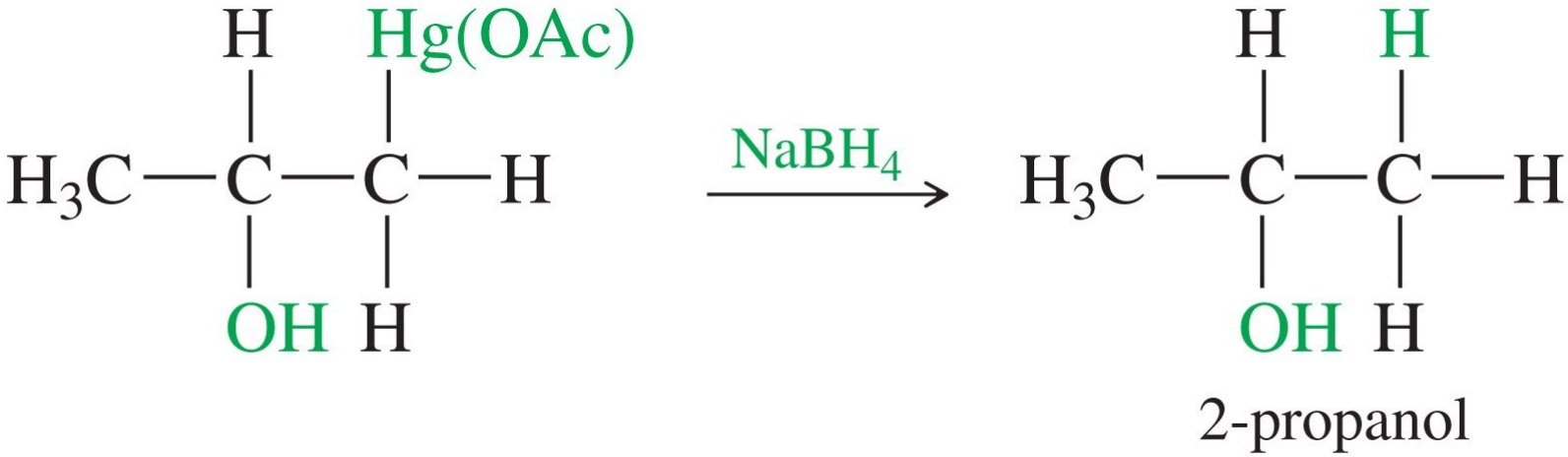
Demercuration Reaction



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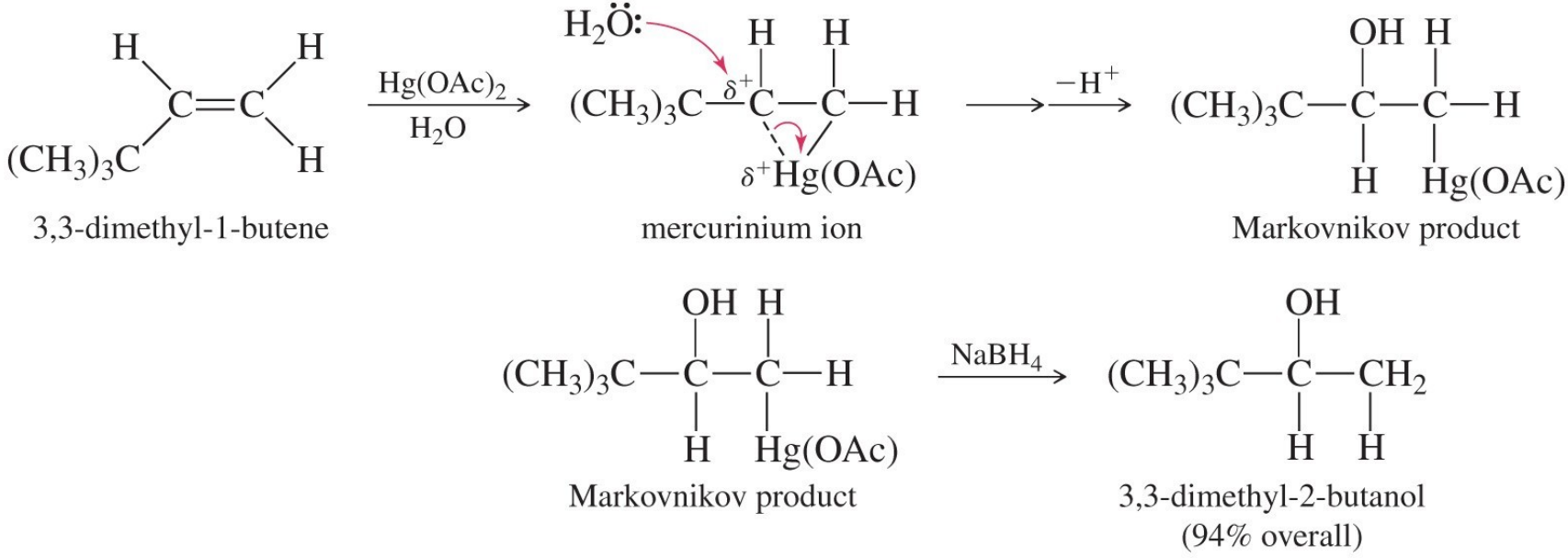
- In the demercuration reaction, a hydride furnished by the sodium borohydride (NaBH4) replaces the mercuric acetate.
- The oxymercuration-demercuration reaction gives the Markovnikov product with the hydroxy group on the most substituted carbon.

Oxymercuration–Demercuration of 3,3,-Dimethyl-1-butene



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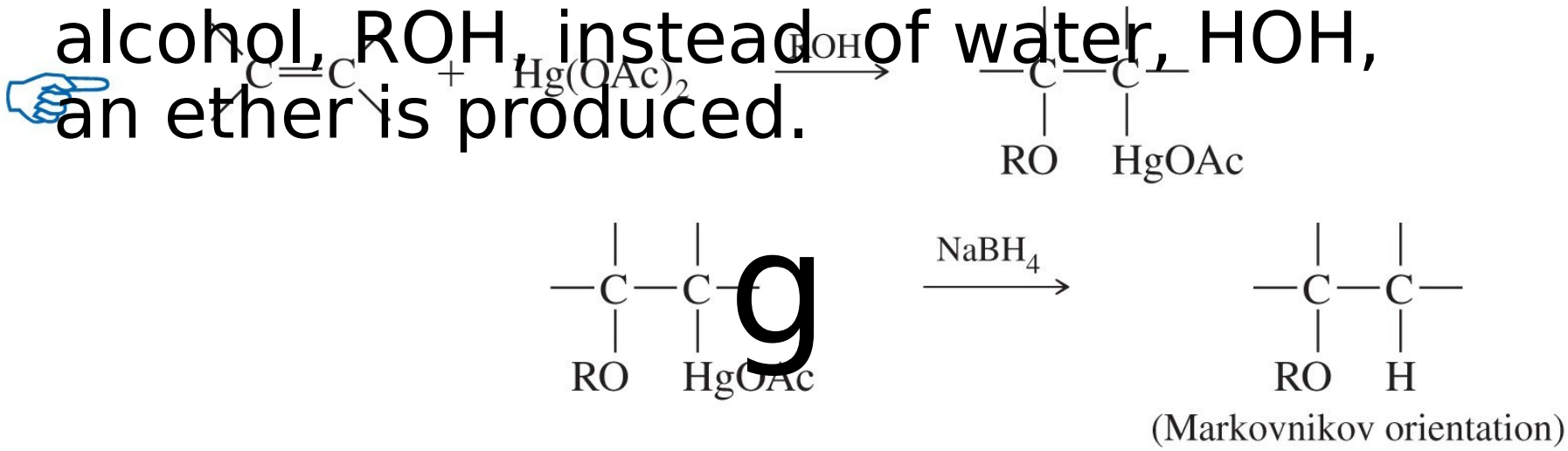
The reaction does not suffer from rearrangements because there is no carbocation intermediate.

Oxymercuration Alcohol addition

Alkoxymercuration–Demercuration

The method is an alcohol, ROH, instead of water, HOH, an ether is produced.



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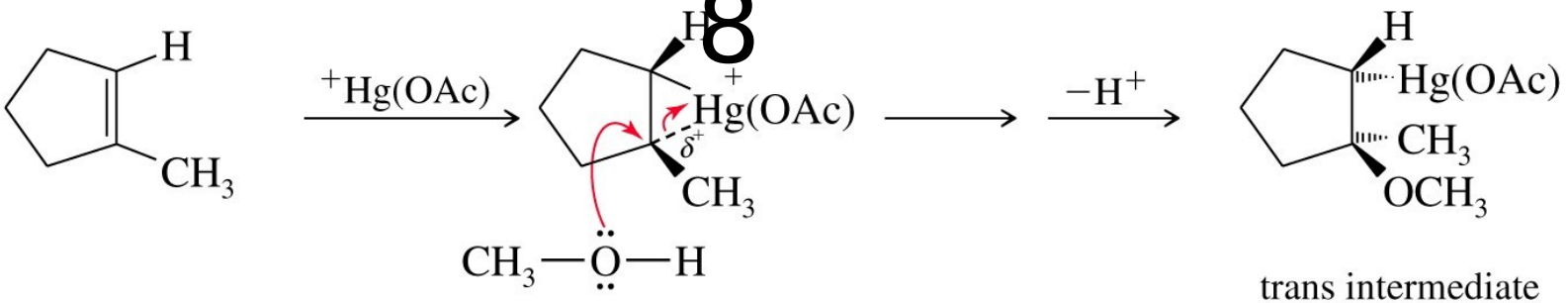
Solved Problem 3

Show the intermediates and products that result from alkoxymercuration–demercuration of 1-methylcyclopentene, using methanol as the solvent.

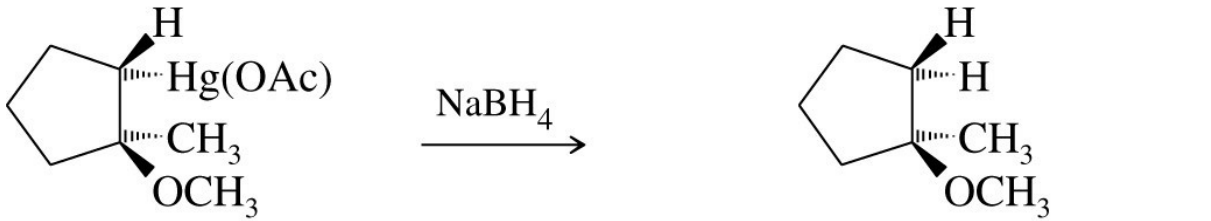
Solution

Mercuric acetate adds to 1-methylcyclopentene to give the cyclic mercurinium ion. This ion has a considerable amount of positive charge on the more substituted tertiary carbon atom. Methanol attacks this carbon.



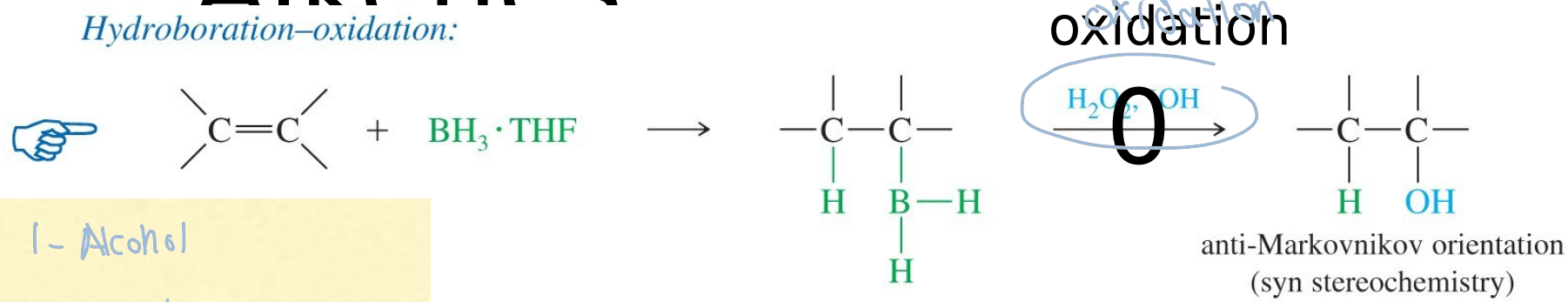
1-methylcyclopentene — mercurinium ion — trans intermediate (product of anti addition)

Reduction of the intermediate gives the Markovnikov product, 1-methoxy-1-methylcyclopentane.



intermediate — 1-methoxy-1-methylcyclopentane

Hydroboration of Alkenes



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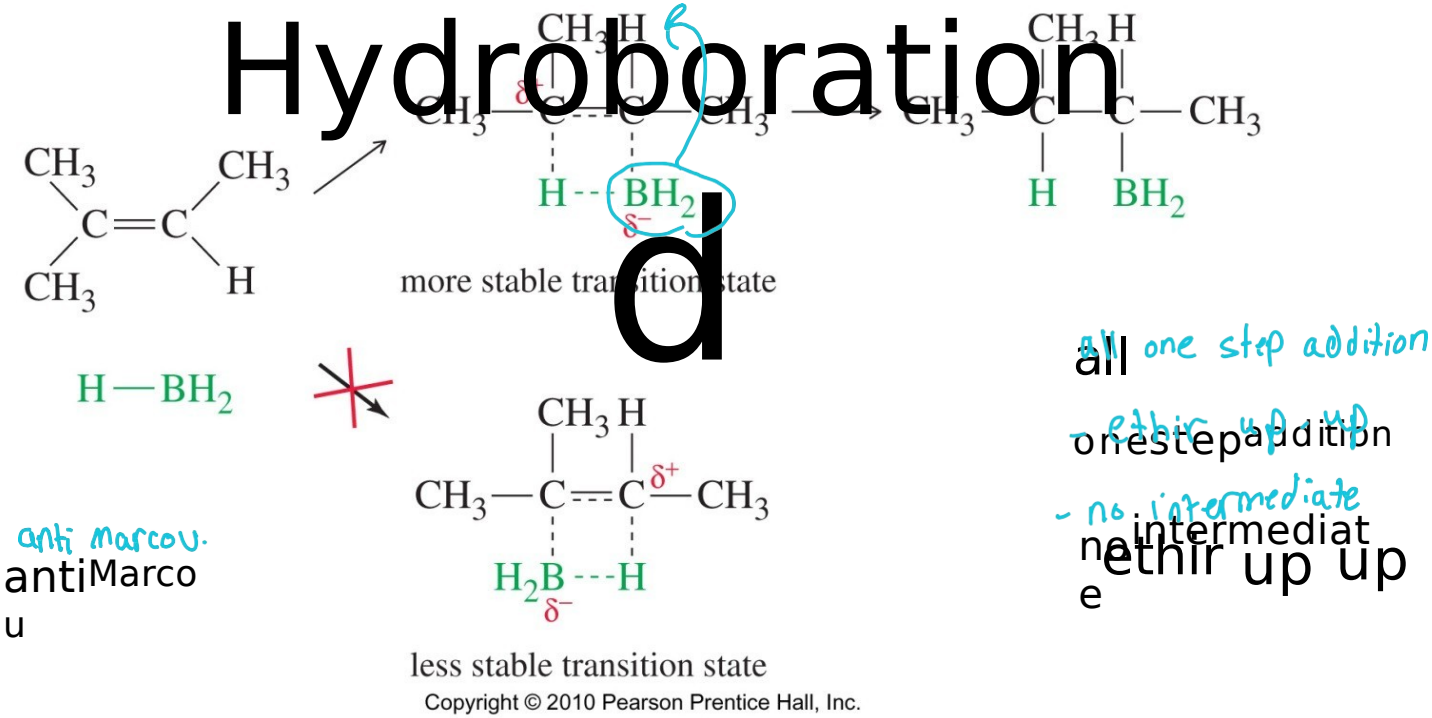
- The reaction adds water across the double bond with anti-Markovnikov orientation.
- BH3 (borane) is a strong Lewis acid.
- Diborane (B2H6) is a dimer of borane and it is in equilibrium with a small amount of BH3.
- BH3•THF is the most commonly used form of borane.

Mechanism of Hydroboration



d

all one step addition

- either up up

- no intermediate

all
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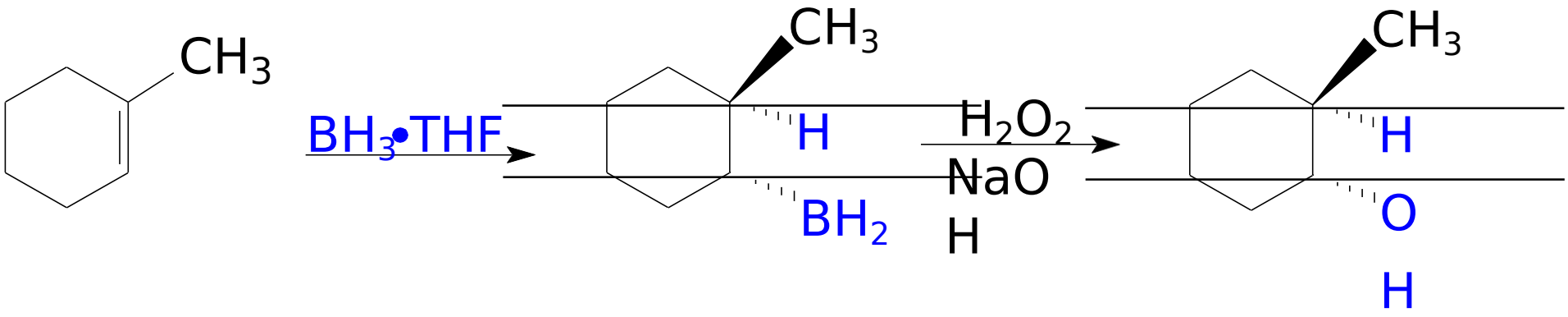
u

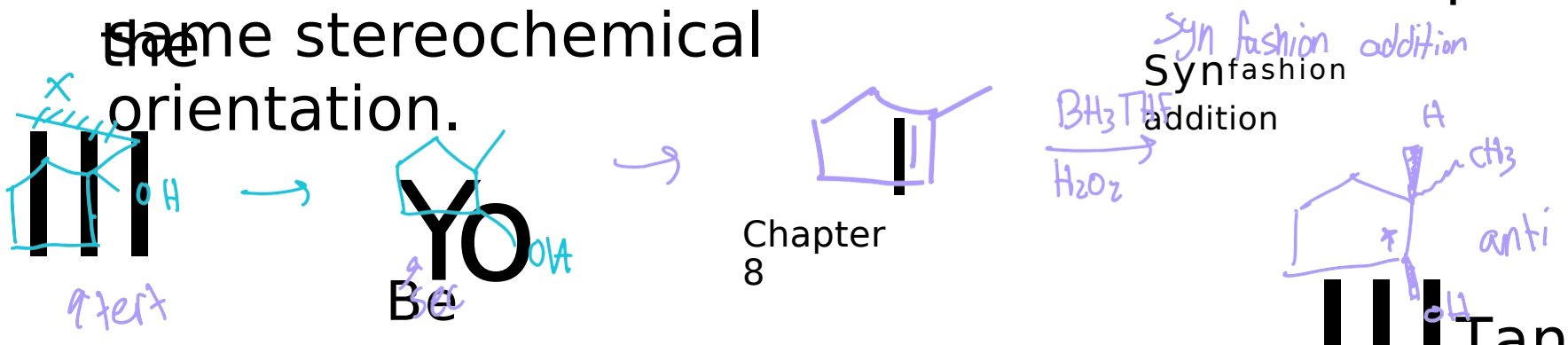
- Borane adds to the double bond in a single step, with boron adding to the less substituted carbon and hydrogen adding to the more highly substituted
- carbon.

This orientation places the partial positive charge in the transition state on the more highly substituted carbon atom.

Stereochemistry of Hydroboration



- The hydroboration steps adds the hydrogen and the boron to the same side of the double bond (***syn addition***).
- When the boron is oxidized, the OH will keep the same stereochemical orientation.

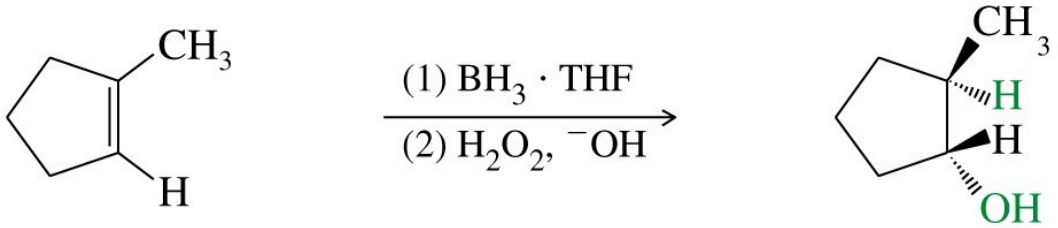


Solved Problem 4

Show how you would convert 1-methylcyclopentanol to 2-methylcyclopentanol.

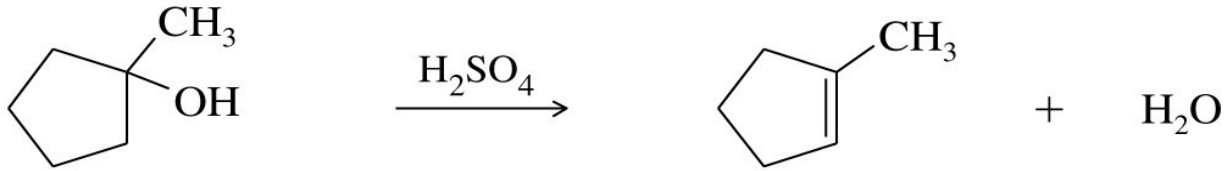
Solution

Working backward, use hydroboration–oxidation to form 2-methyl cyclopentanol from 1- methylcyclopentene. The use of (1) and (2) above and below the reaction arrow indicates individual steps in a two-step sequence.



1-methylcyclopentene *trans*-2-methylcyclopentanol

The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer. This stereochemical result is discussed in Section 8-7C. 1-Methylcyclopentene is the most substituted alkene that results from dehydration of 1-methylcyclopentanol. Dehydration of the alcohol would give the correct alkene.

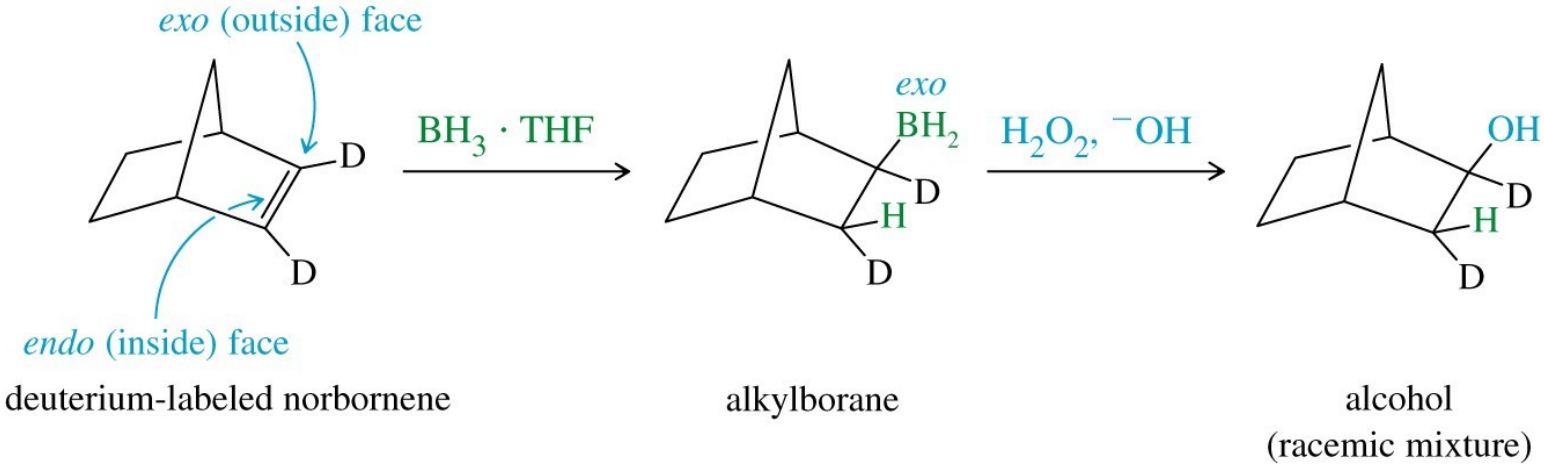


1-methylcyclopentanol 1-methylcyclopentene

Solved Problem 5

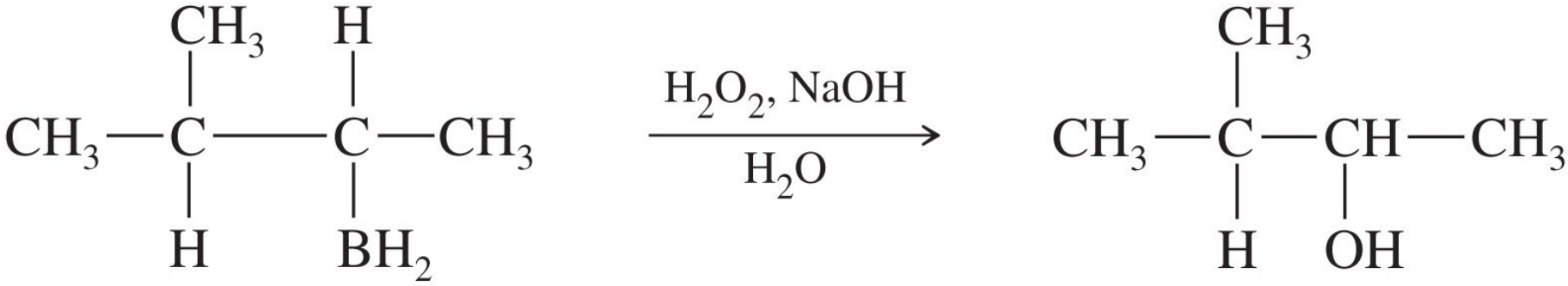
A norbornene molecule labeled with deuterium is subjected to hydroboration–oxidation. Give the structures of the intermediates and products.

Solution



The syn addition of BH3 across the double bond of norbornene takes place mostly from the more accessible outside (exo) face of the double bond. Oxidation gives a product with both the hydrogen atom and the hydroxyl group in exo positions. (The less accessible inner face of the double bond is called the endo face.)

Oxidation to Alcohol



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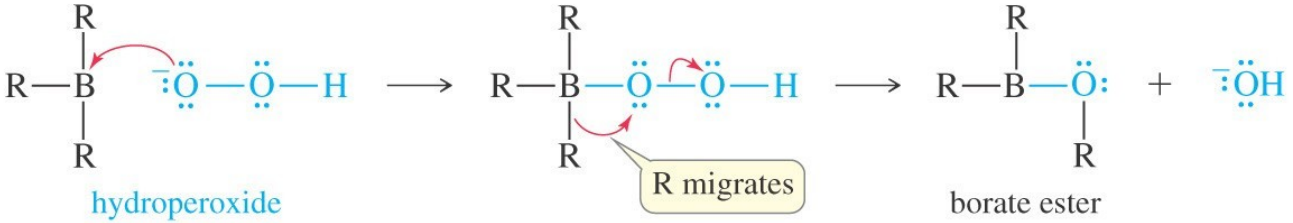
- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.

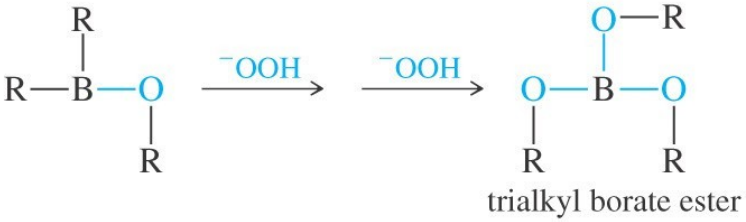
Oxidation of a Tri

Formation of hydroperoxide ion

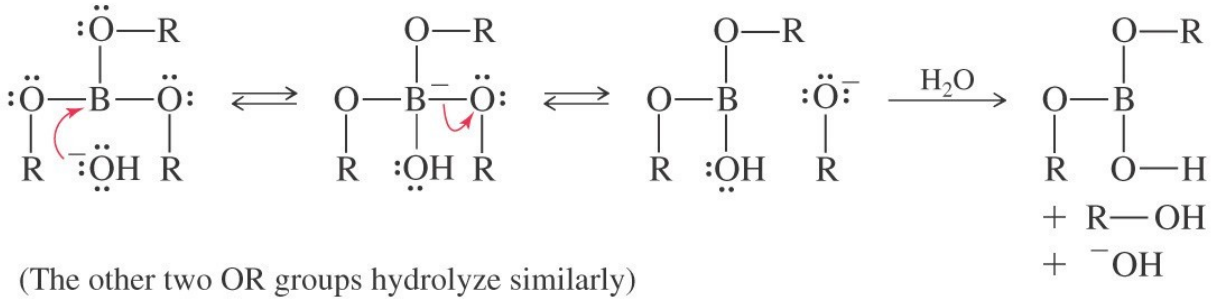
Addition of hydroperoxide and migration of the alkyl group



Twice more to oxidize the other two alkyl groups



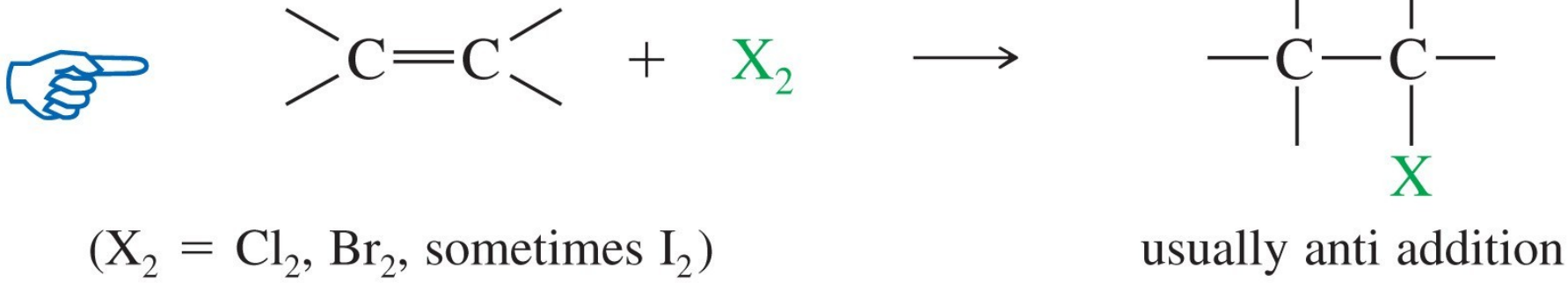
Hydrolysis of the borate ester



Addition of Halogens

important

he genrate Pair of enationers



(X_2 = Cl_2, Br_2, sometimes I_2) usually anti addition

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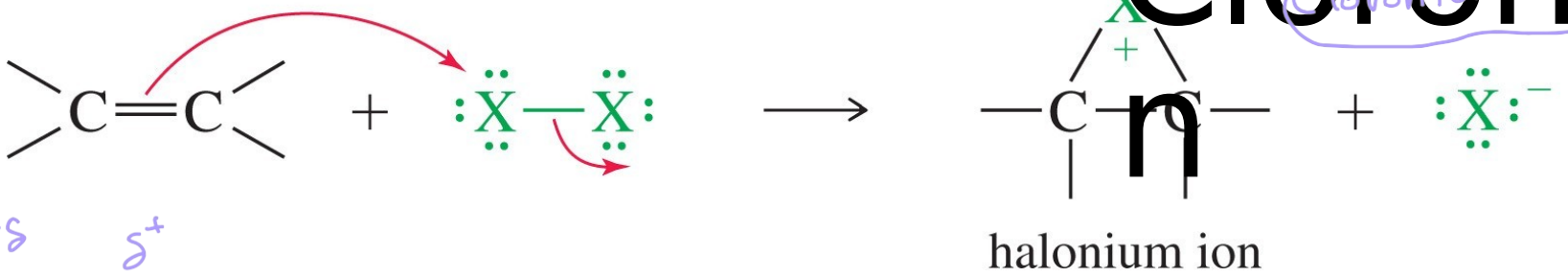
- Cl2, Br2, and sometimes I2 add to a double bond to form a vicinal dibromide.
- This is an anti addition of halides.

Faron

Mechanism of Halogen Addition to Alkene

bromonium br

Cloronio n



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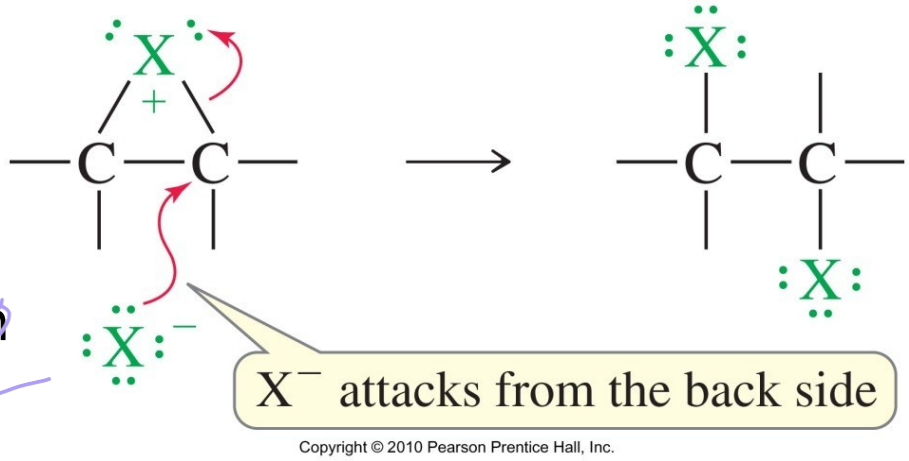
Eye s

different reaction between cis and trans



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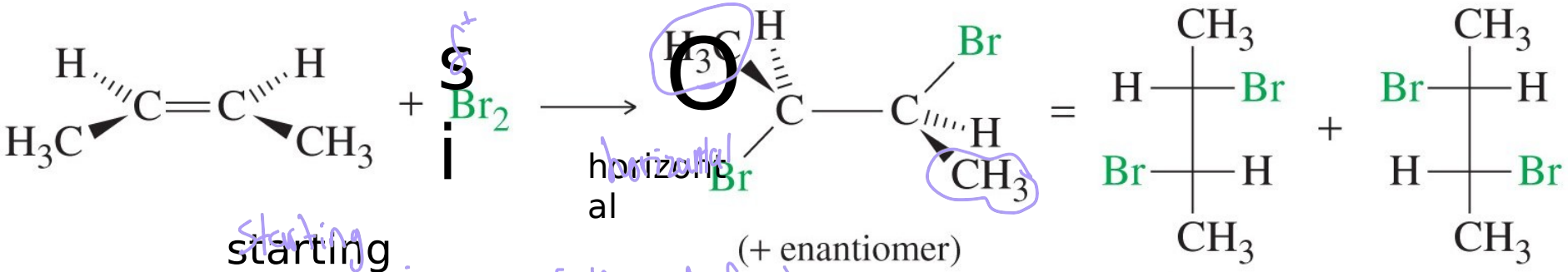
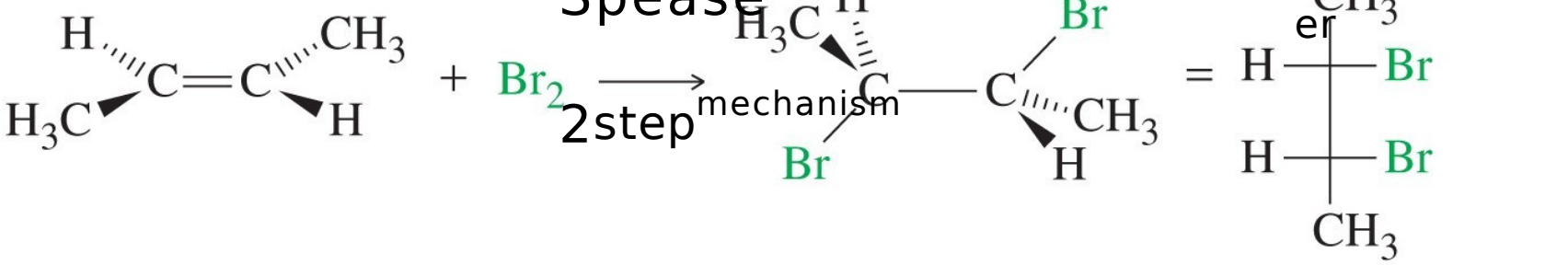
yes

- The intermediate is a three-membered ring called the halonium ion.

Examples of



cis-2-butene



trans-2-butene

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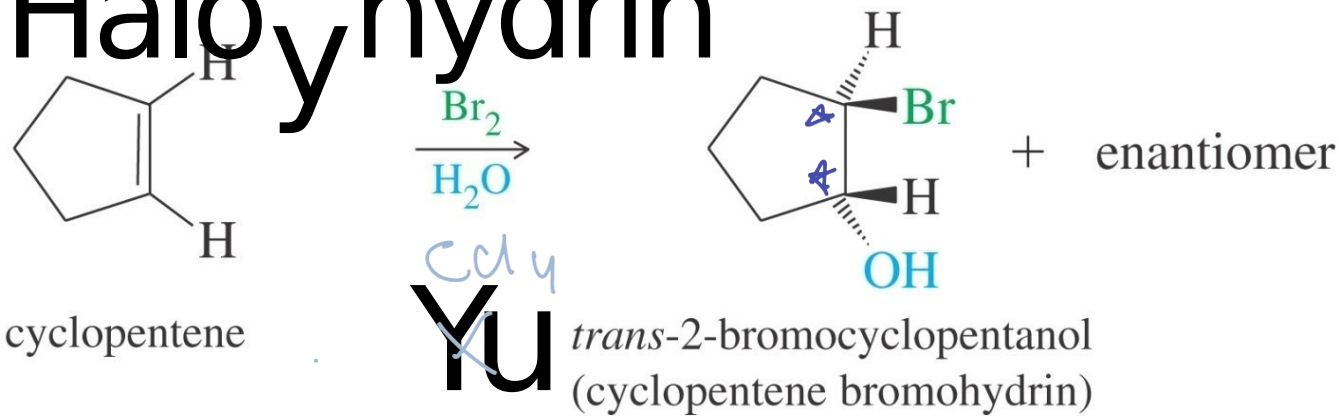
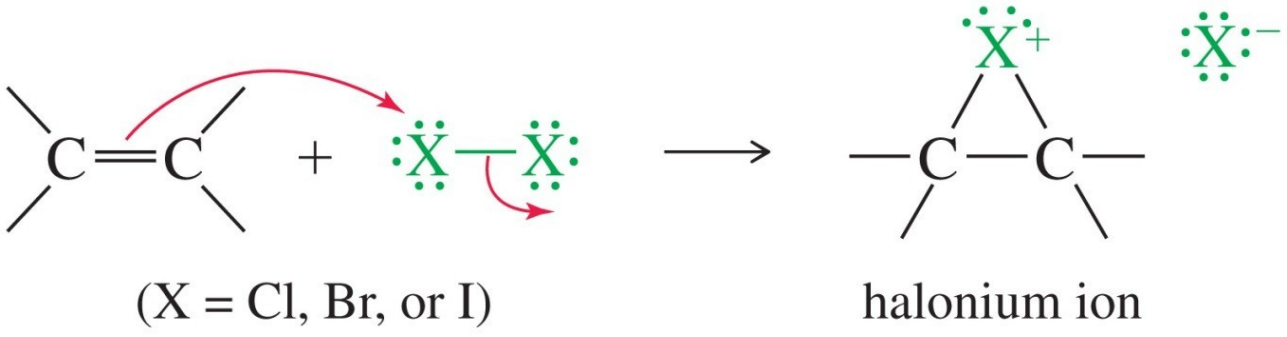
Formation of Halohydrin



- If a halogen is added in the presence of water, a halohydrin is formed.
- Water is the nucleophile.
- This is a Markovnikov addition: The bromide (electrophile) will add to the less substituted carbon.

Mechanism of Halohydrin Formation



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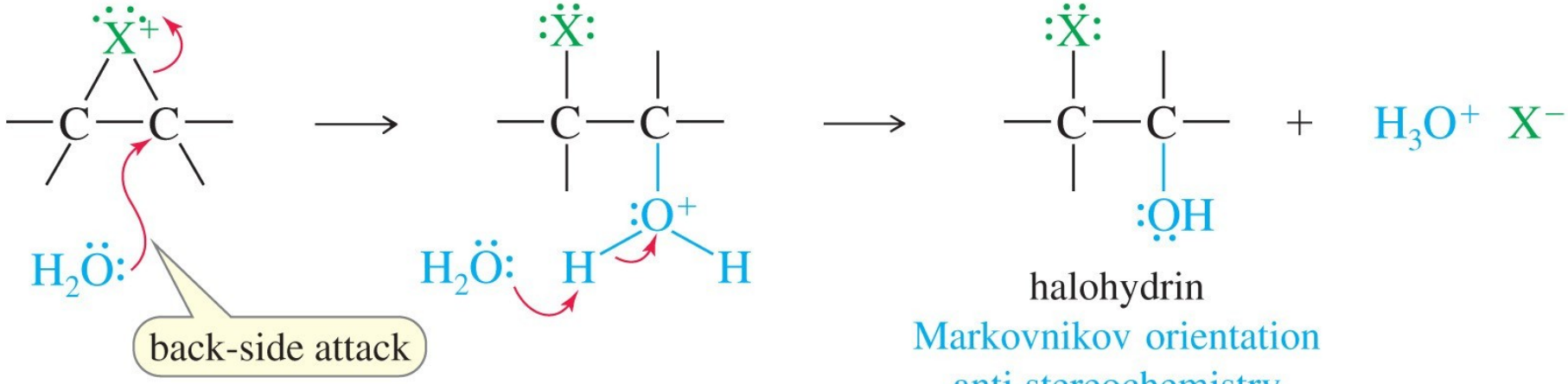

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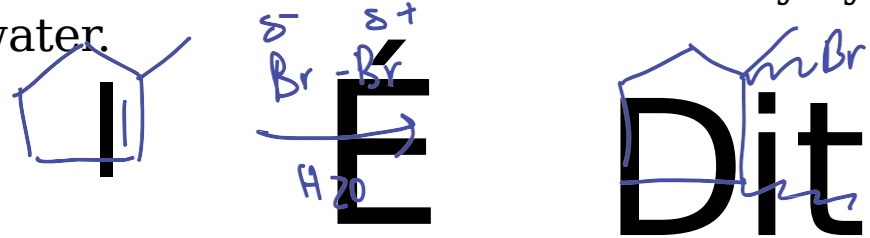
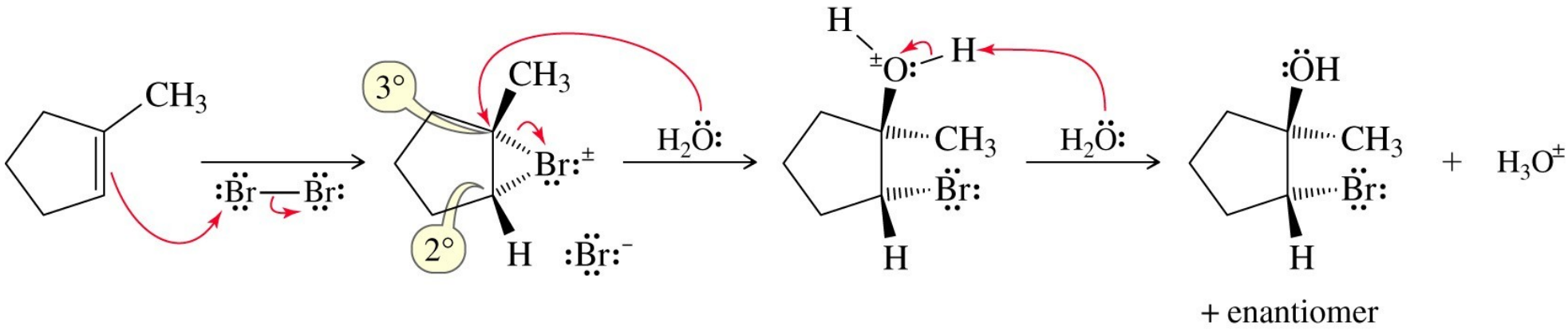
Solved Problem 6

Propose a mechanism for the reaction of 1-methylcyclopentene with bromine water.



Solution

1-Methylcyclopentene reacts with bromine to give a bromonium ion. Attack by water could occur at either the secondary carbon or the tertiary carbon of the bromonium ion. Attack actually occurs at the more substituted carbon, which bears more of the positive charge. The product is formed as a racemic mixture.

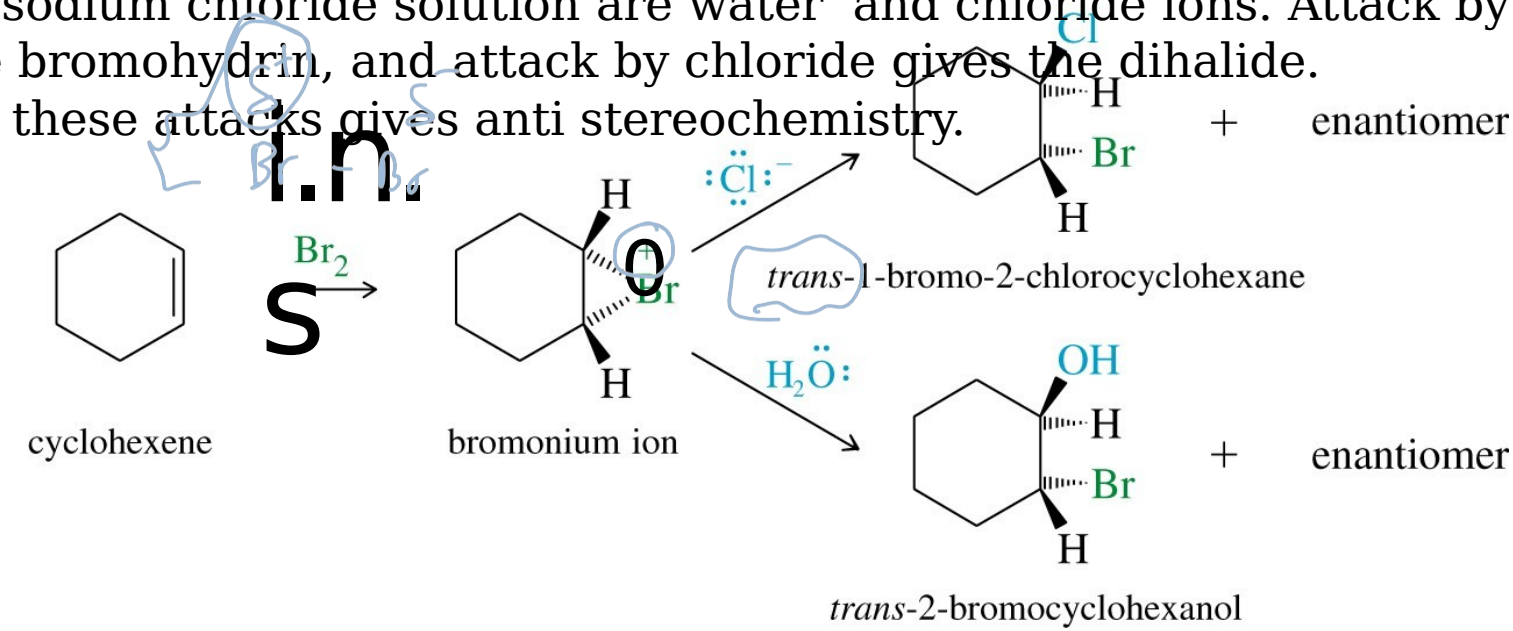


Solved Problem 7

When cyclohexene is treated with bromine in saturated aqueous sodium chloride, a mixture of *trans*-2-bromocyclohexanol and *trans*-1-bromo-2-chlorocyclohexane results. Propose a mechanism to account for these two products.

Solution

Cyclohexene reacts with bromine to give an intermediate bromonium ion, which will react with any available nucleophile. The most abundant nucleophiles in saturated aqueous sodium chloride solution are water and chloride ions. Attack by water gives the bromohydrin, and attack by chloride gives the dihalide. Either of these attacks gives anti stereochemistry.



Hydrogenation of Alkenes

Example

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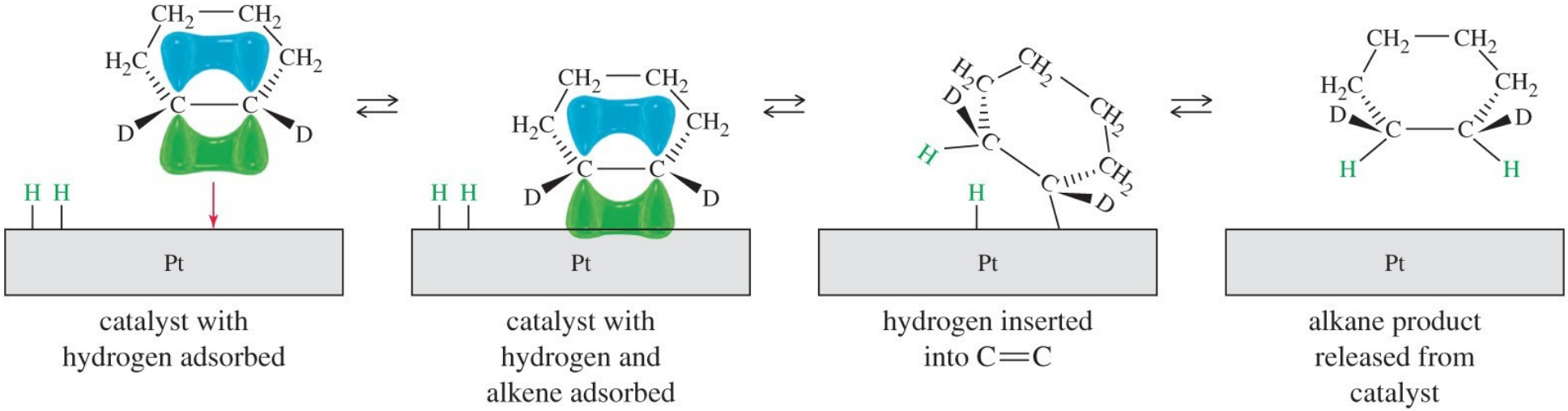
- Hydrogen (H2) can be added across the double bond in a process known as ***catalytic hydrogenation***.
- The reaction only takes place if a catalyst is used. The most commonly used catalysts are palladium (Pd), platinum (Pt), and nickel (Ni), but there are other metals that work just as well.
- Syn addition of hydrogen.

Mechanism of Catalytic


Pt
catalyst with hydrogen adsorbed
catalyst with hydrogen and alkene adsorbed
hydrogen inserted into C=C
alkane product released from catalyst

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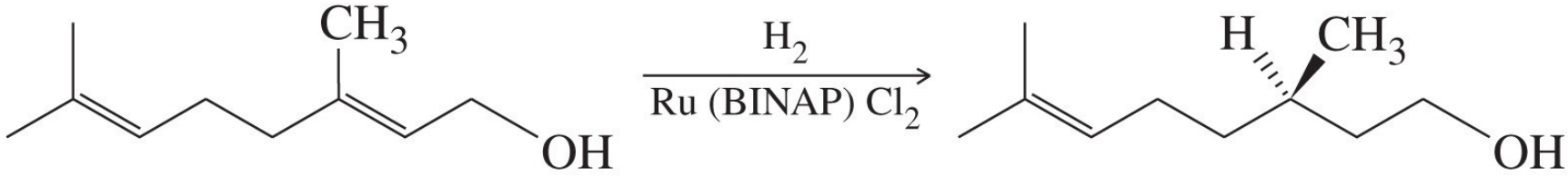
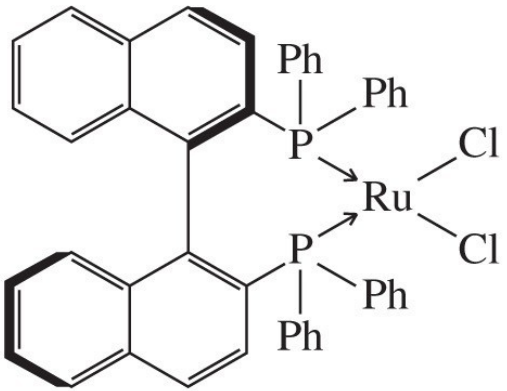
- The hydrogen and the alkene are adsorbed on the metal surface.
- Once adsorbed, the hydrogens insert across the same face of the double bond and the reduced product is released from the metal.
- The reaction has a syn stereochemistry since both hydrogens will add to the same side of the double bond.

Chiral Hydrogenation



Ru(BINAP)Cl_2 =



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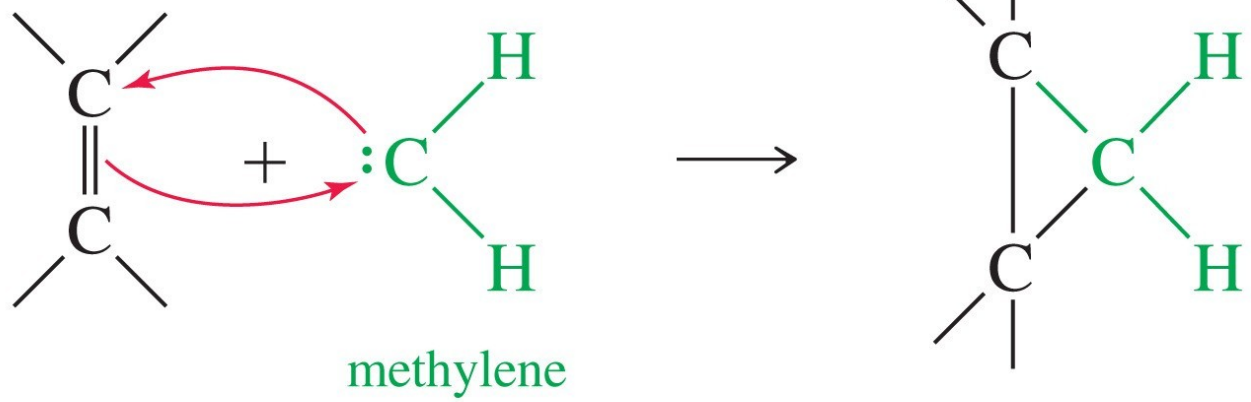
- Rhodium and ruthenium phosphines are effective homogeneous catalysts for hydrogenation.
- Chiral ligands can be attached to accomplish asymmetric induction, the creation of a new asymmetric carbon as mostly one enantiomer.

Addition of



methylene

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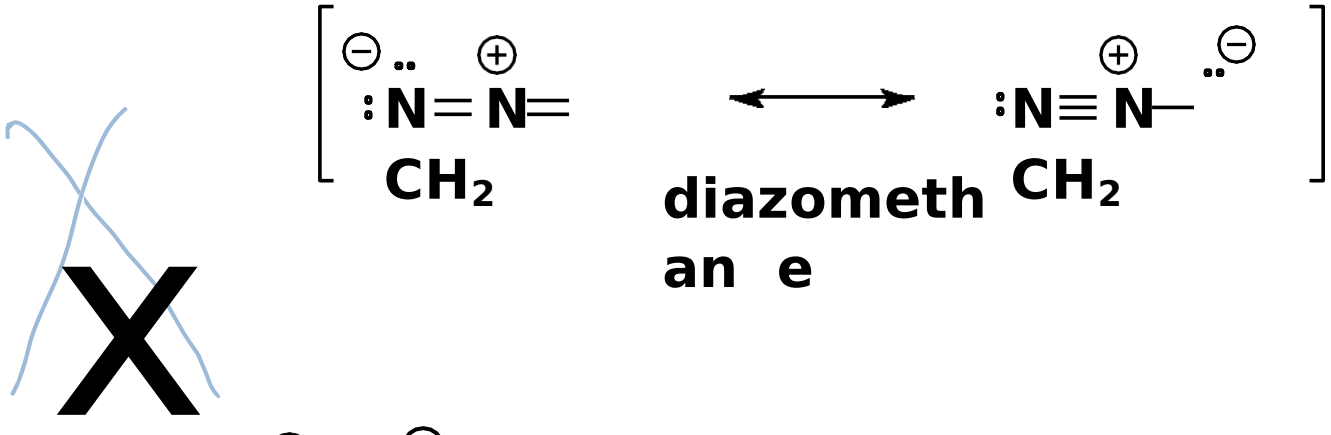
- The nsertion of the —CH2 group into a double bond produces a cyclopropane ring.
- Three methods:
  - Diazomethane (CH3N2, UV light or heat).
  - Simmons–Smith (CH2I2 and Zn(Cu)).
  - Alpha elimination of a haloform (CHX3, NaOH, H2O).

Carbenes: Diazomethane Method

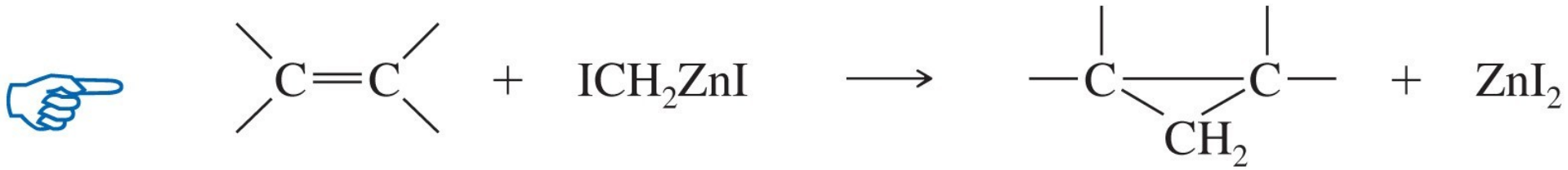


Problems with diazomentane:

1. Extremely toxic and explosive.
2. The carbene can insert into C—H bonds too.

Simmons–Smith Reaction

Best method for preparing cyclopropanes.



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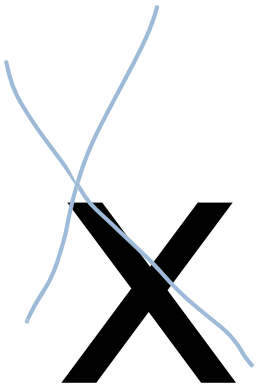
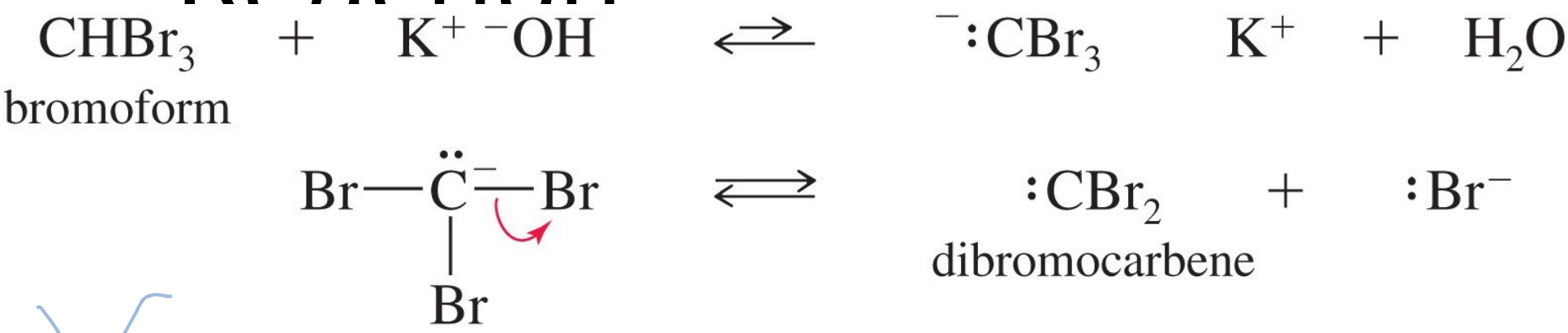


CH2I2 + Zn(Cu) □ ICH2ZnI

Simmons–Smith reagent

Alpha Elimination Reaction



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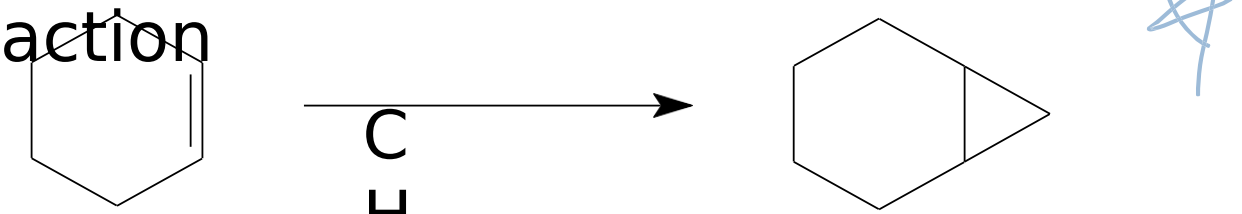
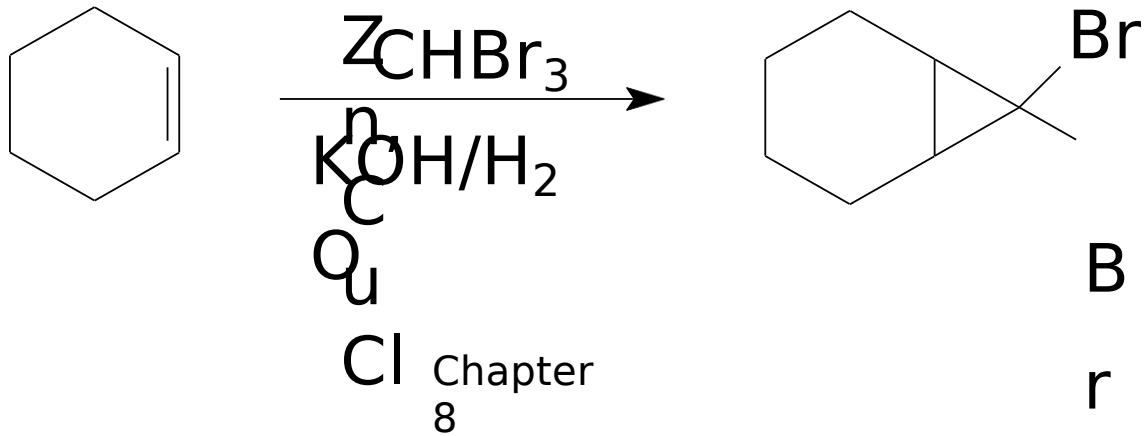
- Xbromoform can be in the presence of a base, dehydrohalogenated to form a chlorocarbene or carbene.

Carbene Examples

Simmons–Smith Reaction

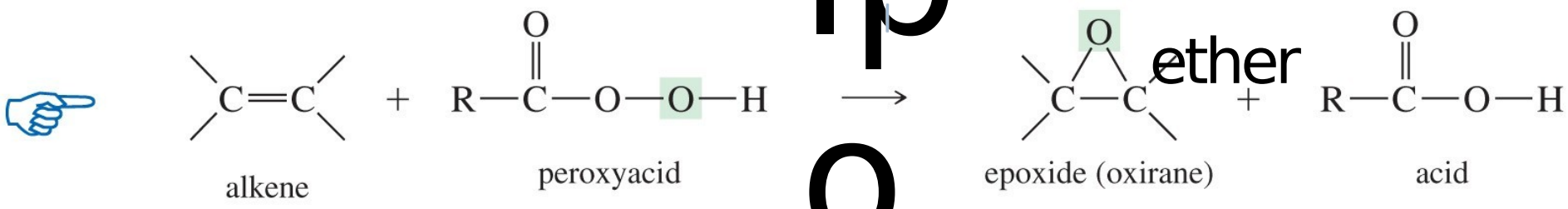




ethers

Epoxidation

cyanic ether



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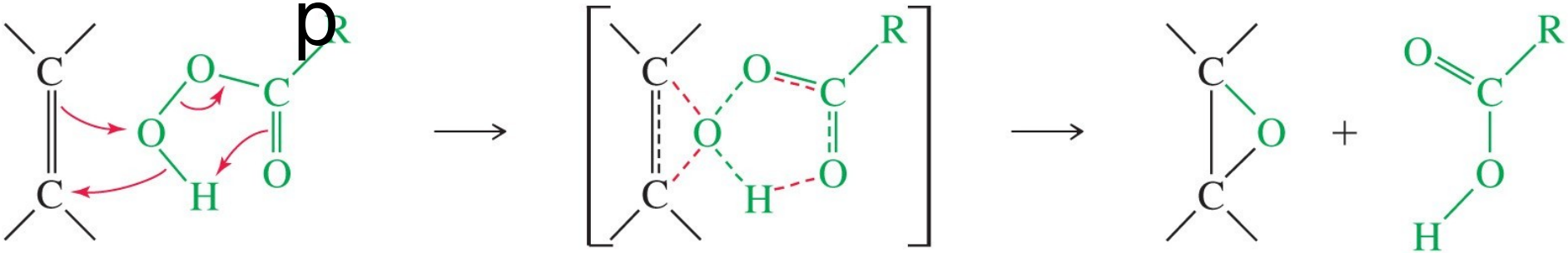
- Alkene reacts with a peroxyacid to form an epoxide (also called oxirane).
- The usual reagent is peroxybenzoic acid.

Mechanism

skip



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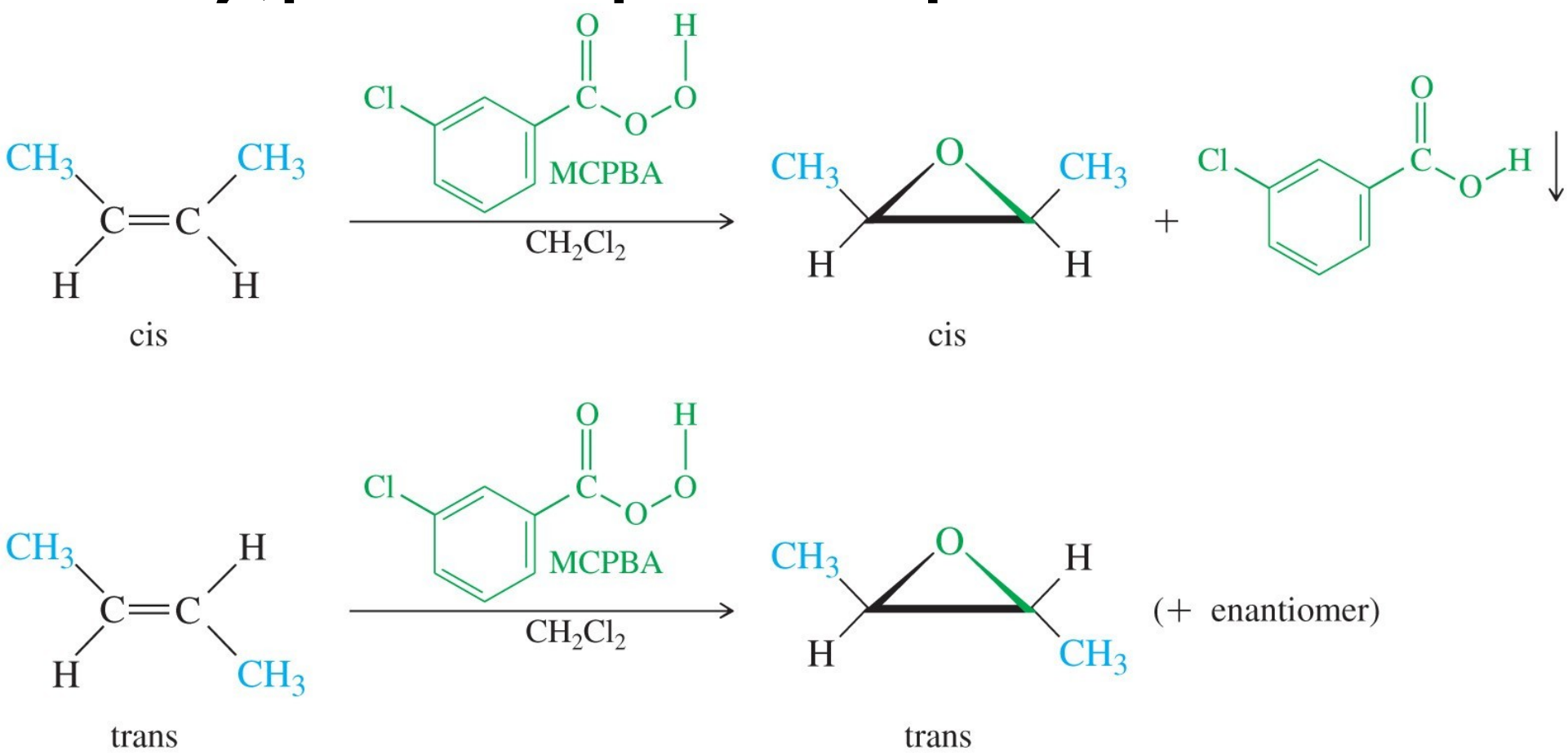
- The peroxyacid and the alkene react with each other in a one-step reaction to produce the epoxide and a molecule of acid.
- The most common peroxyacid used is *meta*-chloroperoxybenzoic acid (MCPBA).

Epoxide



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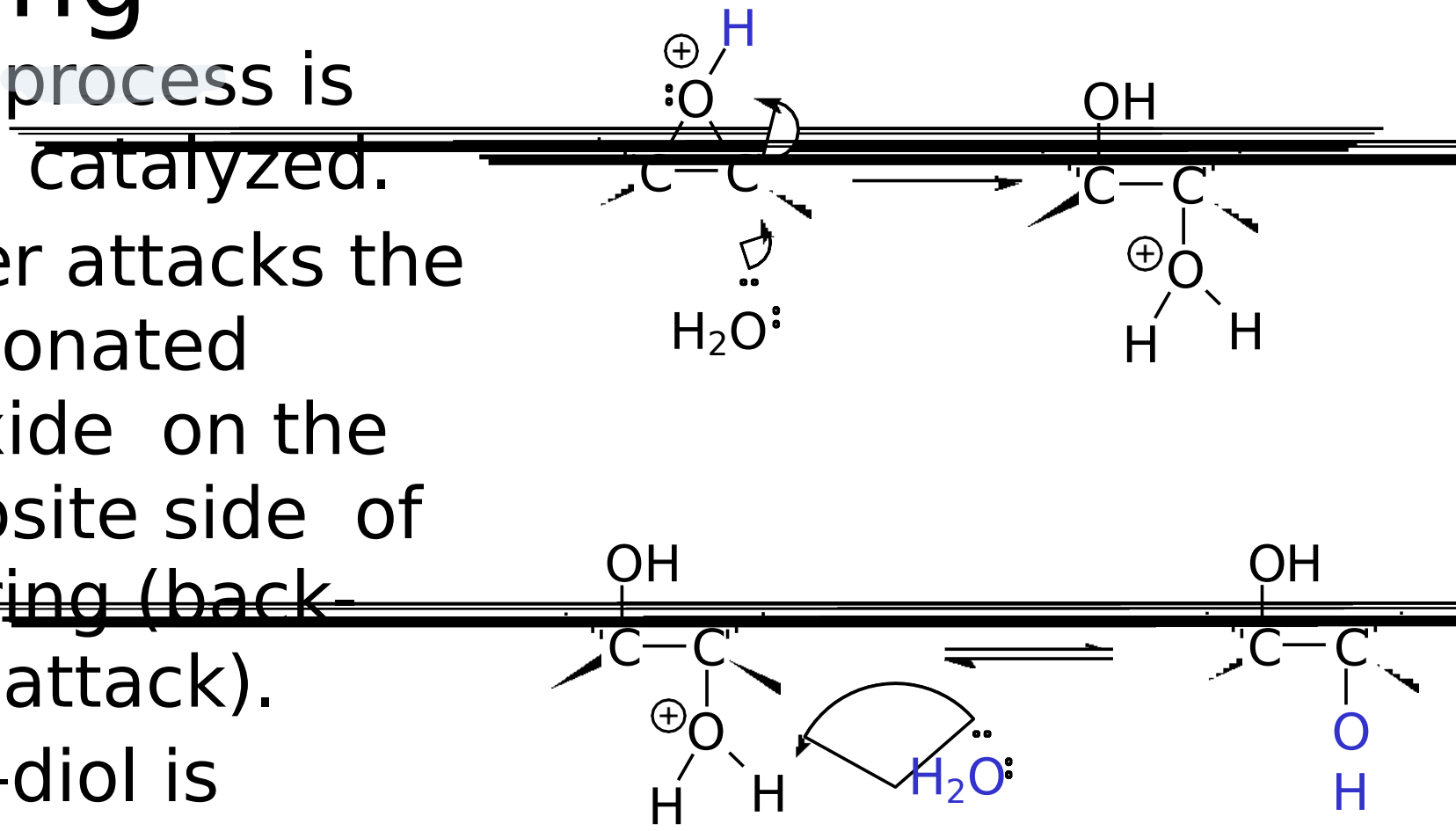
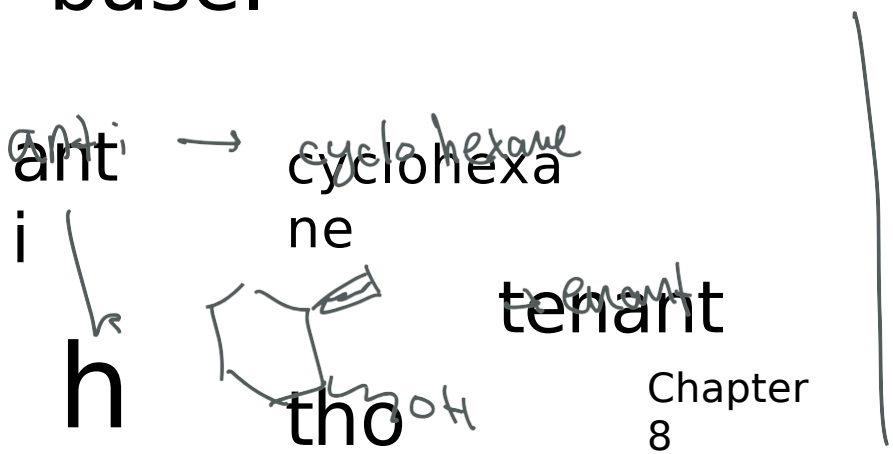
Opening the Epoxide Ring

- This process is acid catalyzed.
- Water attacks the protonated epoxide on the opposite side of the ring (back-side attack).
- Anti–diol is formed.



Syn Hydroxylation of Alkenes

- Alkene is converted to a *syn*-1,2-diol
- Two reagents:
  - Osmium tetroxide, OsO_4, followed by hydrogen peroxide
  - Cold, dilute solution of $KMnO_4$ in base.

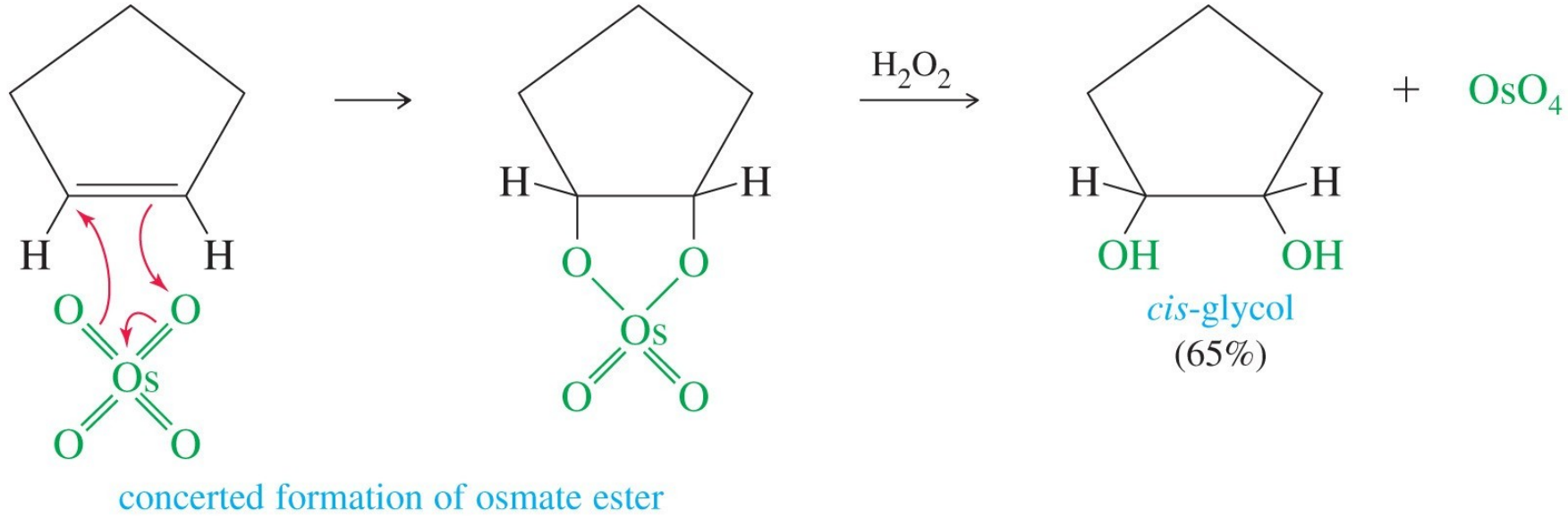


anti → cyclohexane

tenant

Chapter 8

Mechanism with



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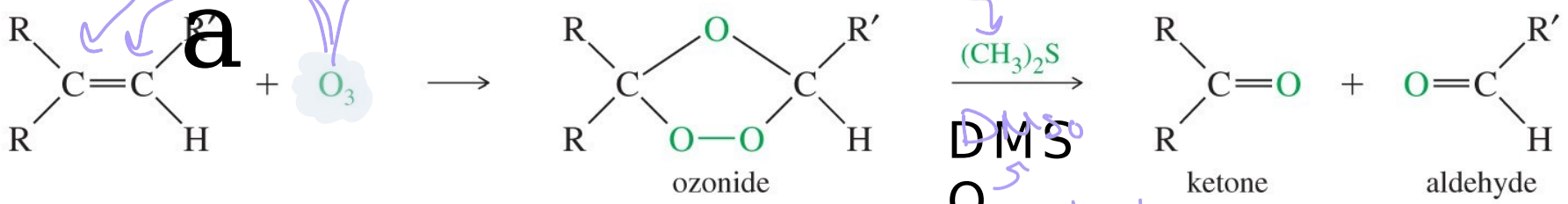
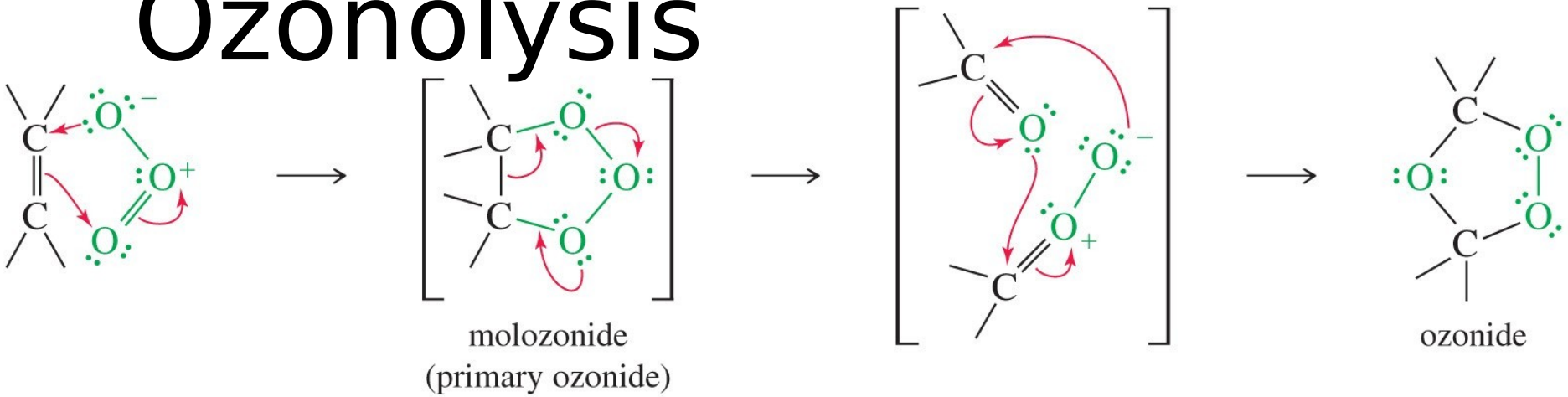
- The osmium tetroxide adds to the double bond of an alkene in a concerted mechanism forming an osmate ester.
- The osmate ester can be hydrolized to produce a *cis*- glycol and regenerate the osmium tetroxide.

Ozonolysis



- Ozone will oxidatively cleave (break) the double bond to produce aldehydes and ketones.
- Ozonolysis is milder than KMnO4 and will not oxidize aldehydes further.
- A second step of the ozonolysis is the reduction of the intermediate by zinc or dimethyl sulfide.

Mechanism of Ozonolysis



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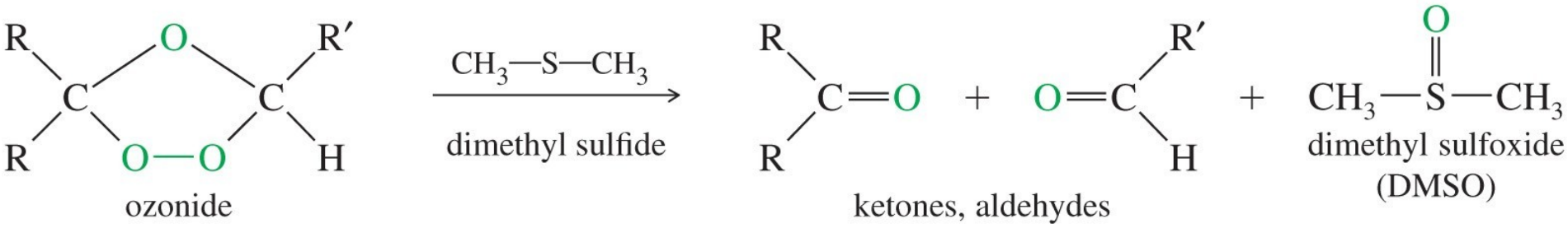
- The ozone adds to the double bond, forming a five-membered ring intermediate called molozonide, which rearranges to form the ozonide.

Reduction of the Ozonide



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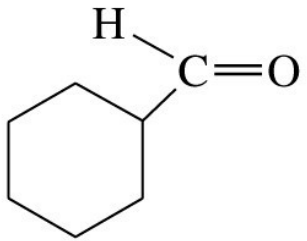
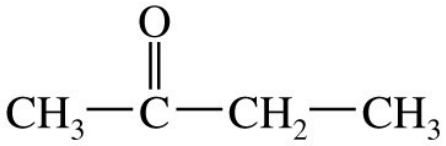
- The ozonide is not isolated, but is immediately reduced by a mild reducing agent, such as zinc or dimethyl sulfide, to give the aldehydes and ketones as the main products.
- When dimethyl sulfide is used the sulfur atom gets oxidized, forming dimethyl sulfoxide (DMSO).

Solved Problem 8

Ozonolysis–reduction of an unknown alkene gives an equimolar mixture of cyclohexanecarbaldehyde and 2-butanone. Determine the structure of the original alkene.



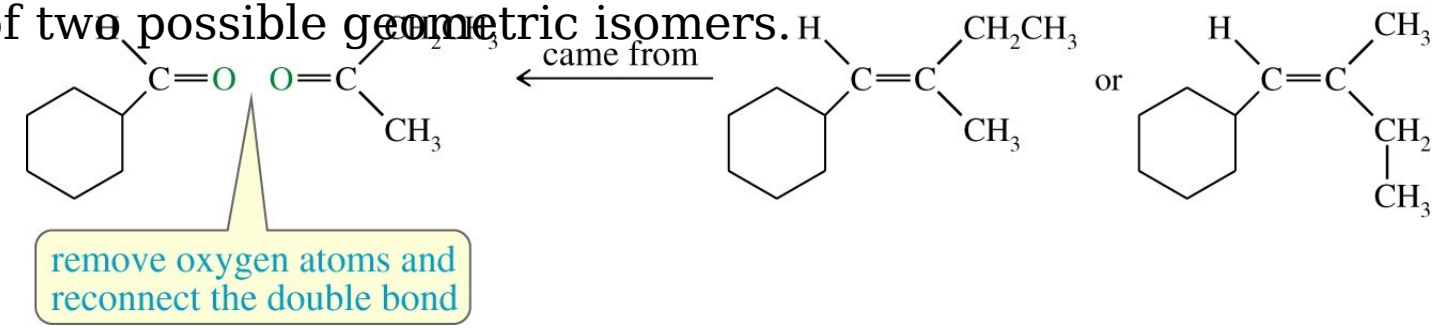
cyclohexanecarbaldehyde



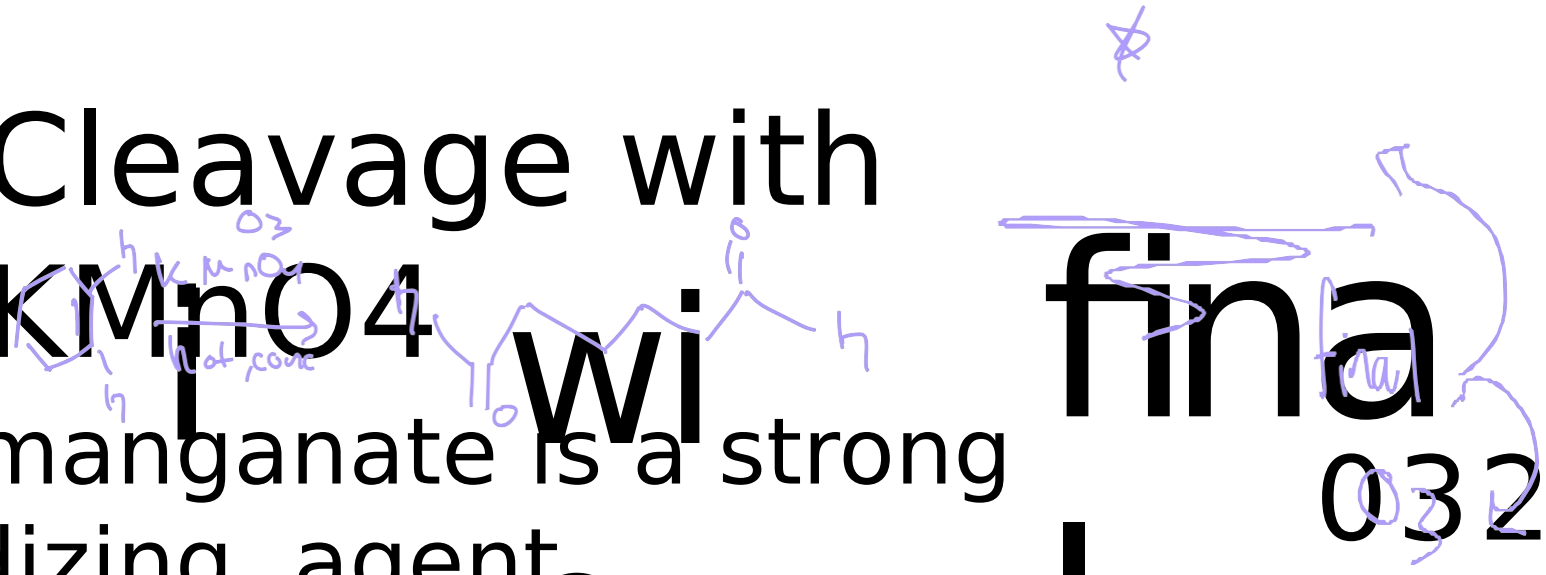
2-butanone

Solution

We can reconstruct the alkene by removing the two oxygen atoms of the carbonyl groups (C=O) and connecting the remaining carbon atoms with a double bond. One uncertainty remains, however: The original alkene might be either of two possible geometric isomers.

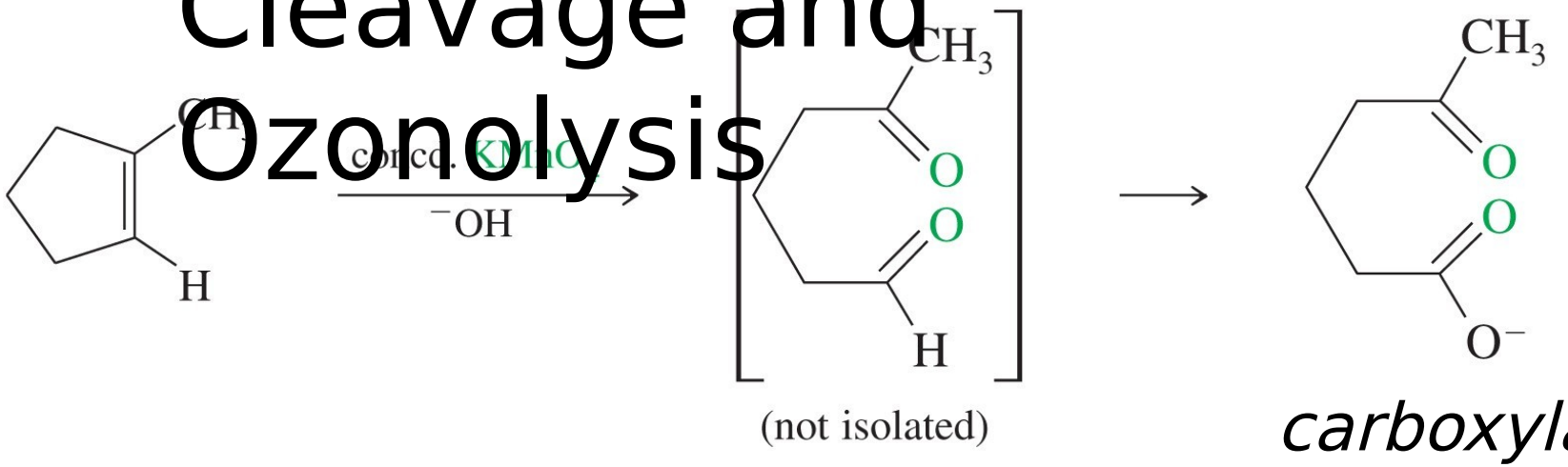


Cleavage with KMnO4

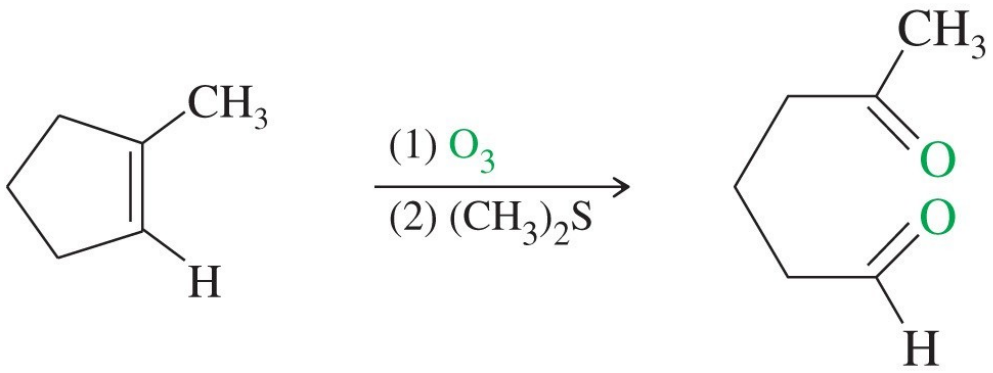


- Permanganate is a strong oxidizing agent.
- Glycol initially formed is further oxidized.
- Disubstituted carbons become ketones.
- Monosubstituted carbons become carboxylic acids.
- Terminal =CH2 becomes CO2.

Comparison of Permanganate Cleavage and Ozonolysis



carboxylate



Aldehydes can be isolated.

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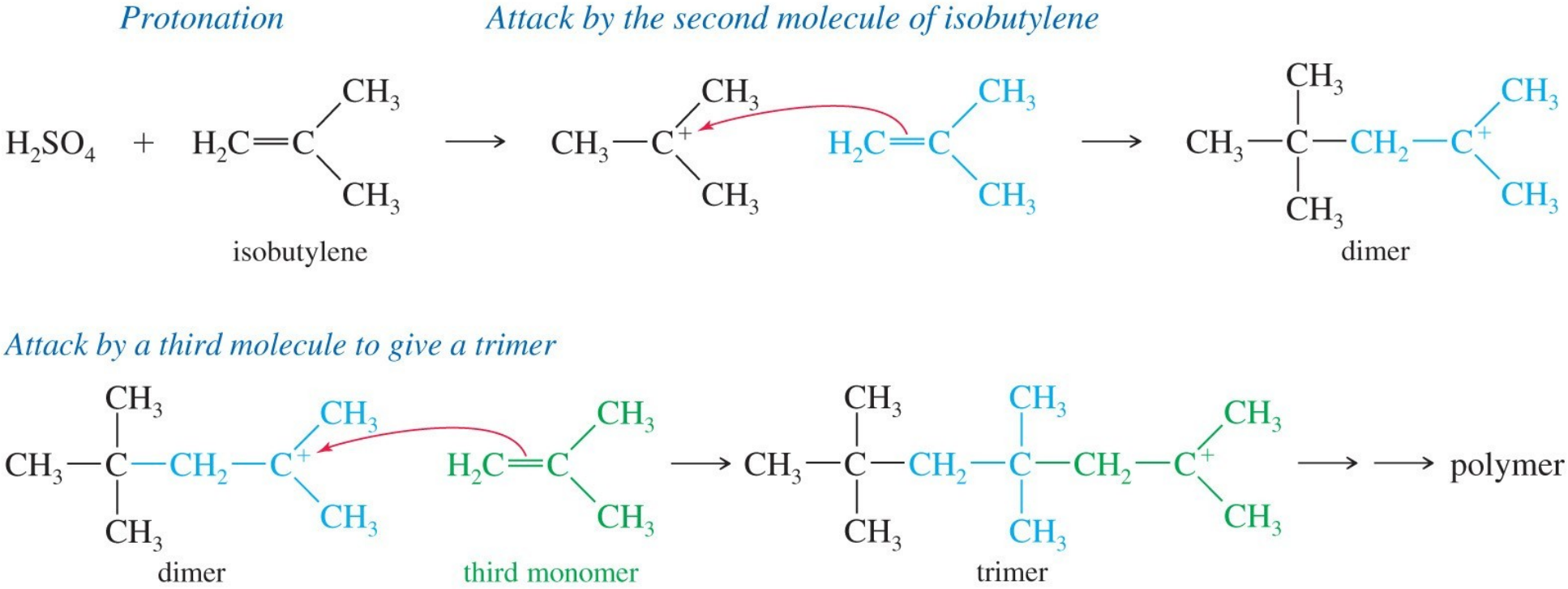
Polymerization

- An alkene (monomer) can add to another molecule like itself to form a chain (polymer).
- Three methods:
  - Cationic, a carbocation intermediate
  - Free radical
  - Anionic, a carbanion intermediate (rare)

Cationic Polymerization



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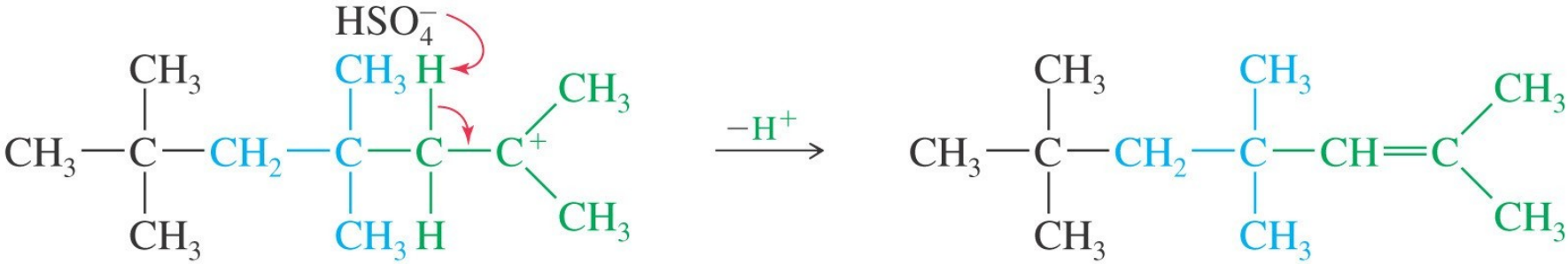
Termination Step of Cationic Polymerization



- The chain growth ends when a proton is abstracted by the weak base of the acid used to initiate the reaction.
- The loss of a hydrogen forms an alkene and ends the chain growth so this is a termination step.